

Noble Metal based Catalysts for Natural Gas Steam Reforming
Activity, Endurance and Kinetics

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Noble Metal based Catalysts for Natural Gas Steam Reforming

Activity, Endurance and Kinetics

A thesis submitted in partial fulfillment of the requirement of degree
of

Doctorate in Chemical Engineering

at

**Department of APPLIED SCIENCE AND TECHNOLOGY
(DISAT)**

POLITECNICO DI TORINO

by

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In supervision of

Prof. Stefania Specchia

XXVII Cycle

Academic year 2012-2014



This Research has been produced under the Project of UESTP by the Higher Education Commission, Pakistan at the Department of Applied Science (DISAT) of Politecnico di Torino, Italy.

December 2014

Dedication

To my family

Ami, Dady, Dada Abu, Dadi amman

Ayesha, Asma, Bhai, Aapa, Mamu, Rabi, Anu

Acknowledgement

My foremost gratitude to Almighty Allah, the most beneficent the most merciful, for His countless blessings on me in every walk of life.

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Abstract

This thesis illustrates catalytic activity, stability and intrinsic kinetics of methane steam reforming (MSR) reaction over noble metal catalysts. The main objective of this thesis is to evaluate a best performing catalyst based on the maximization of H₂ production and minimization of CO in the synthesis gas produced from MSR reaction.

The noble metal catalysts tested towards MSR reaction were Rh, Ru and Pt supported on different reducible and irreducible oxides. The oxides (CeO₂, MgO and Al₂O₃) used in this work were synthesized from their nitrite precursor by Simultaneous combustion synthesis (SCS) while Nb₂O₅ was prepared by heat treatment of Niobic acid obtained from Companhia Brasileira de Metalurgia e Mineração (CBMM, Brasil). In all the catalysts the noble metals were deposited on the support by wetness impregnation method, except Pt/CeO₂ which was prepared by one shoot SCS method. All the prepared catalysts were calcined under different calcination regimes. The best performing catalysts were characterized by different techniques BET, CO chemisorption, porosimetry, XRD, XPS, ICP, TEM and SEM analyses. Efforts have been made to correlate the catalytic activity with the physical characterization.

All the catalysts prepared were initially screened by MSR reaction in a tubular fixed bed quartz reactor of 4mm ID containing 30mg of catalyst diluted with 50mg of inert. For catalytic screening and stability test the feed was introduced at a weight hourly space velocity of 20 NLh⁻¹g⁻¹cat and steam to carbon ratio 3-4 depending upon the catalyst. The results obtained from basic screening of the catalysts were analyzed in terms of methane conversion, H₂ produced in dry reformat and CO₂ selectivity. Among all the catalysts tested towards MSR only two were chosen based on initial screening, Rh/CeO₂ and Pt/CeO₂, for the further test concerning catalyst stability.

The stability of Rh/CeO₂ and Pt/CeO₂ catalysts was determined based on daily start up and shut down cycle (DSS) with a 6h performance period. The Pt/CeO₂

catalyst was tested for a total of 150 h in which 100h performance was with DSS in N_2 environment while 50h of catalyst activity with DSS in reaction environment. The Rh/CeO₂ catalyst was tested for a total of 25 h catalyst activity with DSS in N_2 environment. Additionally the Rh/CeO₂ catalyst was also tested in 100h continuous ageing. Both the catalysts showed good results in terms of catalyst activity and stability during the time period. As Rh/CeO₂ catalyst showed good activity during 100h continuous endurance this catalyst was chosen to evaluate the intrinsic kinetics of methane steam reforming.

For the kinetics test firstly the heat and mass transfer limitations were evaluated both experimentally and theoretically. The reactor was operated in an integral mode and no inert was used in feed for the kinetic experiments. The effect of WHSV at constant S/C 3 on the methane conversion and product composition was also determined. The partial pressures of the reactants were varied by varying the steam-to-carbon ratio of the feed. An attempt was made to fit kinetic data obtained using the models available in literature. The kinetic data obtained was perfect fit for the model proposed by Berman, and the activation energy of Rh/CeO₂ was found to be 38.6 kJ/mol.

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Chapter 1 : Introduction

1.1 Natural gas

Natural gas is a fossil fuel formed from exposure of heat and pressure to buried layers of plants and animals over thousands of years. Natural gas contains more than 80% methane.

Natural gas is usually burned to generate electricity and the main products of combustion are CO_2 and water vapours the same compounds human exhale. Coal and oil on the other hand have higher carbon ratio and high nitrogen and sulphur content which makes coal and oil structure much more complex. Burning of oil and coal, due to their structural complexity, releases high level of harmful emissions including NO_x and SO_x . Ash particles also results from oil and coal combustion and contribute to air pollution. Natural gas combustion do not produce any ash content and very low levels of CO, CO_2 and other reactive hydrocarbons. Natural gas is a non-renewable energy source. It is the cleanest of fossil fuels as evident from the chart below.

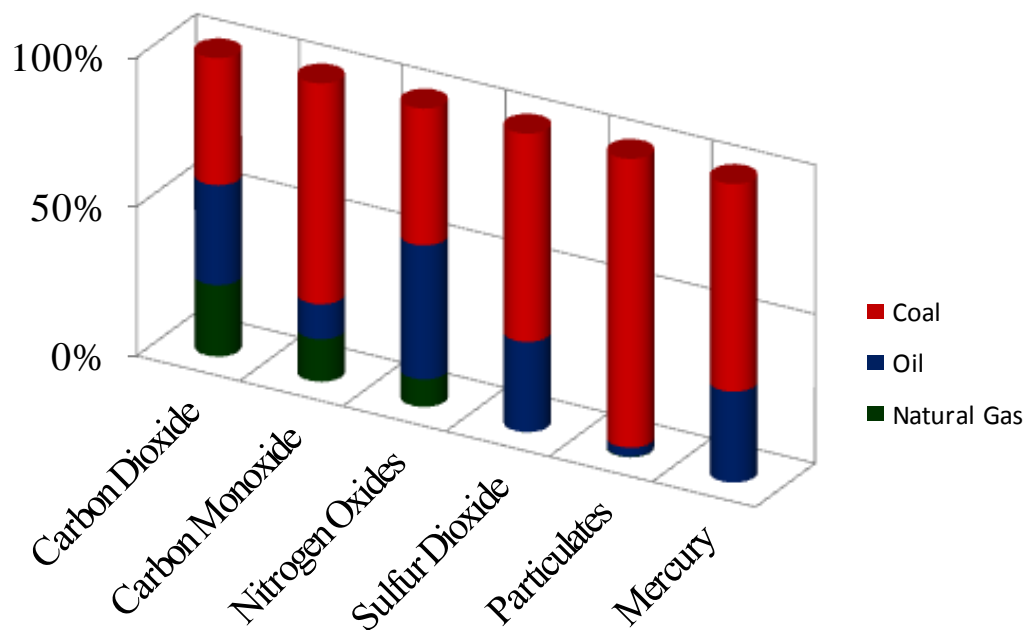


Figure 1.1: Comparison of emission from Natural gas, Coal and oil¹

Despite of all the natural gas advantages, it contains more than 80% methane which is the second most important greenhouse gas². Methane is potentially more dangerous than CO₂ because of its greater radiative forcing produced per molecule. However methane exists in atmosphere in far less concentrations than CO₂ and is measured in ppb rather than ppm³. Also methane has a only 10 year residence time in atmosphere compared with hundreds of years of CO₂.

The natural sources of methane along with the natural sinks are presented in methane cycle in **Figure 1.2**.

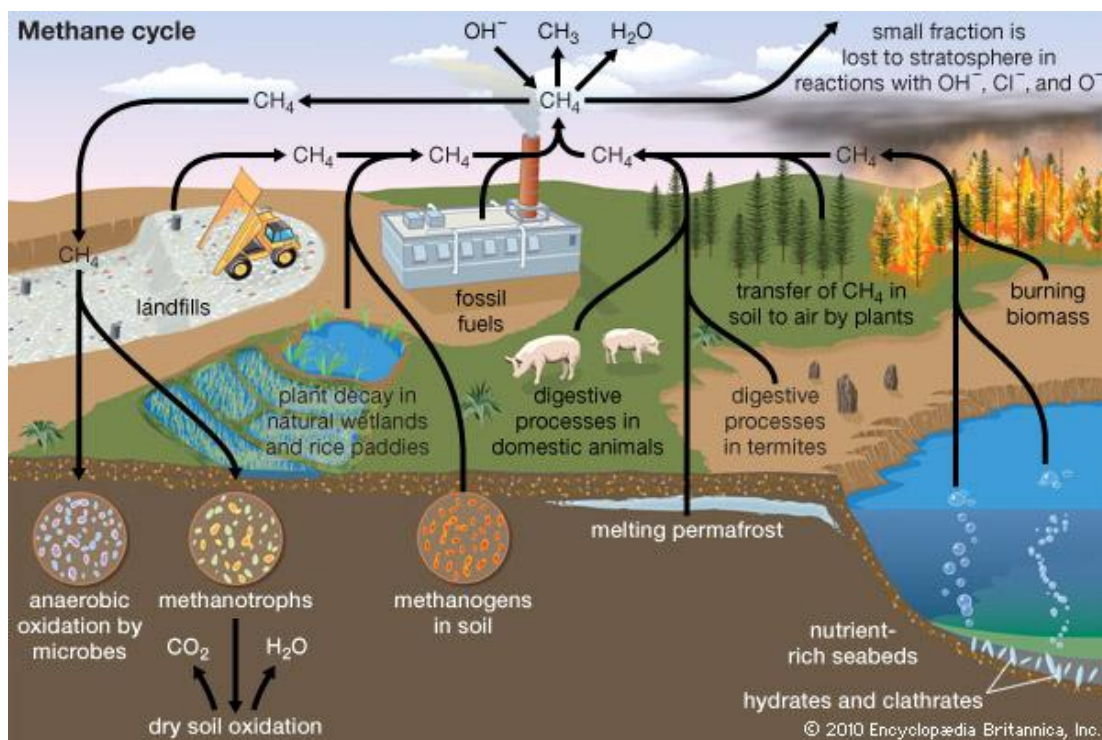


Figure 1.2: The Methane Cycle³

The greatest advantage of natural gas is being a source of syngas. Methane has the simplest structure among all the hydrocarbons so it produces syngas: a mixture of hydrogen and carbon monoxide with minimum amount of other byproducts. Hydrogen is the cleanest of all the fuels with high energy content. Industrially hydrogen is produced mainly from methane present in natural gas. The major route for hydrogen production is via catalytic steam reforming route.

Figure 1.3 presents the primary energy distribution of the sources to produce hydrogen.

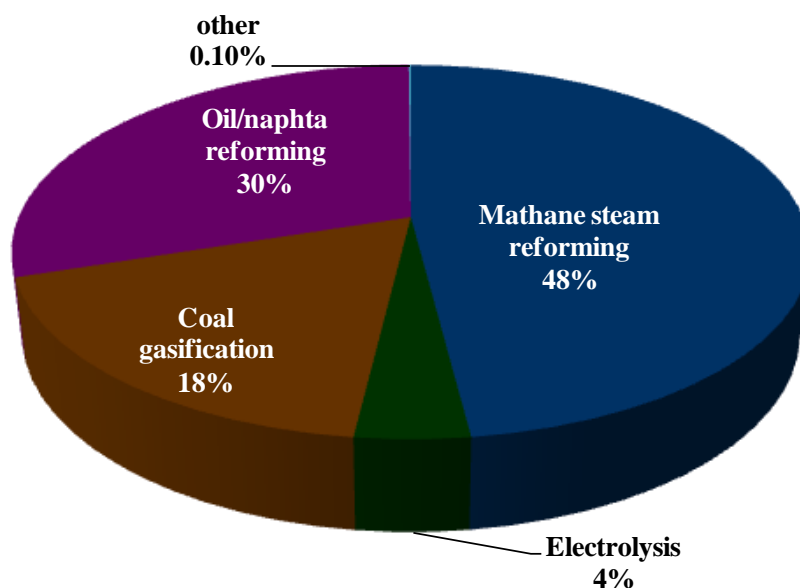


Figure 1.3: Distribution of primary energy sources for hydrogen production⁴.

1.2 Natural gas Reforming Process

The routes of producing syngas from natural gas reforming are as follows;

- i Steam Reforming
- ii Partial oxidation
- iii Autothermal reforming/ Oxidative steam reforming
- iv Dry reforming

1.2.1 Catalytic Steam Reforming:

Steam reforming or methane steam reforming (MSR) is the reaction where steam and hydrocarbons, such as natural gas or refinery feed stock, react in a reformer at temperature of 800–900°C and moderate pressure of around 30 bar, in the presence of metal based catalyst for the production of syngas^{5–8}. Syngas reacts further to give more hydrogen and carbon dioxide via water gas shift (WGS) equilibrium reaction, which is a side reaction in steam reforming. Steam reforming is a catalytic and energy efficient process for producing a H₂ rich

syngas from light hydrocarbons like natural gas, refinery off-gases, LPG or naphtha. The hydrocarbon feedstock is fed to the reformer after being mixed with steam in steam to carbon (S/C) ratios higher than 2.7⁹. This excessive steam is required for completion of reactions as well as avoiding carbon formation^{10,11}.

The main reactions involved in MSR are as follows¹²,



The highly endothermic steam reforming reactions are usually catalyzed by Ni supported on ceramics such as alumina or alumina magnesium spinels^{12,13}. However, the possible utilization of noble metal catalyst is also in progress and reported in literature¹⁴⁻¹⁷.

1.2.2 Partial Oxidation Process

1.2.2.1 Non Catalytic Partial Oxidation:

Non catalytic partial oxidation (NCPO) is a unique technology to produce CO rich syngas from hydrocarbons. The reaction takes place between 1200°C to 1500°C and the exothermic reaction^{7,18} involved is,



However this process is mainly utilized for heavy hydrocarbons reforming. The main utilization of this process is in the following systems⁹

- (i) in H₂ production for refinery applications,
- (ii) synthesis gas production from coal and
- (iii) in electric energy production from petroleum coke and deasphalter bottoms, through large Integrated Gas Turbine Combined Cycles (IGCC)

1.2.2.2 Catalytic Partial Oxidation:

In order to reduce the high temperature requirement for NCPO process the catalytic partial oxidation (CPO) is used^{19,20}. The catalyst employed for partial oxidation reaction reduces the temperature to 800-900°C and is also known as the short contact time catalytic partial oxidation (SCT-CPO). The CPO process is sensitive to sulfur poisoning and can only work efficiently for fuels with sulphur content below 50 ppm⁹.

1.2.3 Autothermal Reforming/ Oxidative Reforming:

Autothermal reforming (ATR) is the combination of partial oxidation and steam reforming^{6,21,22}. Firstly the partial oxidation reaction occurs followed by reforming in the catalyst bed. This reaction is exothermic due to the partial oxidation process. When the ATR uses dry reforming after partial oxidation the H₂:CO molar ratio produced in syngas is 1:1. If steam reforming is employed the H₂:CO molar ratio is 2.5:1. Operating ATR with O/C molar ratios less than 0.7 is generally called OSR²³⁻²⁵.

1.2.4 Dry Reforming:

The reforming of CH₄ with CO₂ produces synthesis gas with a lower H₂/CO ratio than that generated by the widely employed steam/CH₄ reforming reaction.



The two reactions have similar thermodynamic characteristics except that in the case of CO₂/CH₄ reforming there is a greater potential for carbon formation, primarily due to the lower H/C ratio of this system²⁶.

The choice of reforming process affects the thermal efficiency of the plant, plant size and location, plant capital cost, the physical size of downstream gas handling equipment, syngas composition and the downstream conversion process. A comparison of syngas generation technologies using natural gas as feed is shown below in **Table 1.1**.

Table 1.1: Comparison of syngas generation technologies (natural gas feed)⁹

Technology	Advantages	Disadvantages
CPOX	Feed stock desulfurization not required	Very high process operating temperature Usually requires oxygen plant
MSR	Most extensive industrial experience Oxygen not required, lowest process operating temperature Best H ₂ /CO ratio for production of liquid fuels	Highest air emissions More costly than POX and autothermal reformers Recycling of CO and removal of the excess hydrogen by means of membranes
ATR	Lowest process temperature requirement than POX Syngas methane content can be tailored by adjusting reformer outlet temperature	Limited commercial experience Usually requires oxygen plant
MDR	Green house gas CO ₂ can be consumed instead of releasing in to atmosphere Almost 100% of CO ₂ conversion	Formation of coke on catalyst Additional heat is required as the reaction takes place at 873 K

1.3 Research scope and thesis layout:

This thesis presents an experimental and modeling work for H₂ production from methane. The scope of this thesis is categorized in the three Parts:

Part I consists of **Chapter 3** to **Chapter 6** and includes experimental study for the catalytic activity for low-temperature steam reforming of methane over noble metal based catalyst.

Part II consist of **Chapter 7** and **Chapter 8** and deals with the stability and endurance of CeO₂ supported Pt and Rh catalyst

Part III addresses the intrinsic kinetics of MSR reaction over Rh catalyst encircled in **Chapter 9**.

Finally **Chapter 10** summarizes the general conclusions of the research and implies several recommendations for the improvement of the process. Future perspective for the H₂ production process

Part I and **Part II** cover the area of catalysis in terms of catalyst characterization, activity testing, stability, and reaction performance study, while **Part III** envelops the area of catalytic reaction engineering in terms of intrinsic kinetics

This thesis is an assemblage of a series of papers published and/or to be published in the relevant journals on this topic. Every chapter can be seen as a stand-alone research paper. The list of Published papers or the manuscripts in progress is given at the end of the thesis.

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Chapter 2 Experimental

2.1 Methane steam reforming (MSR) plant:

The catalytic activity, stability and kinetics was carried out in a MSR plant which was designed to ensure a flexible system. The flow sheet of MSR plant is presented in **Figure 2.1**. The plant consists of following four sections

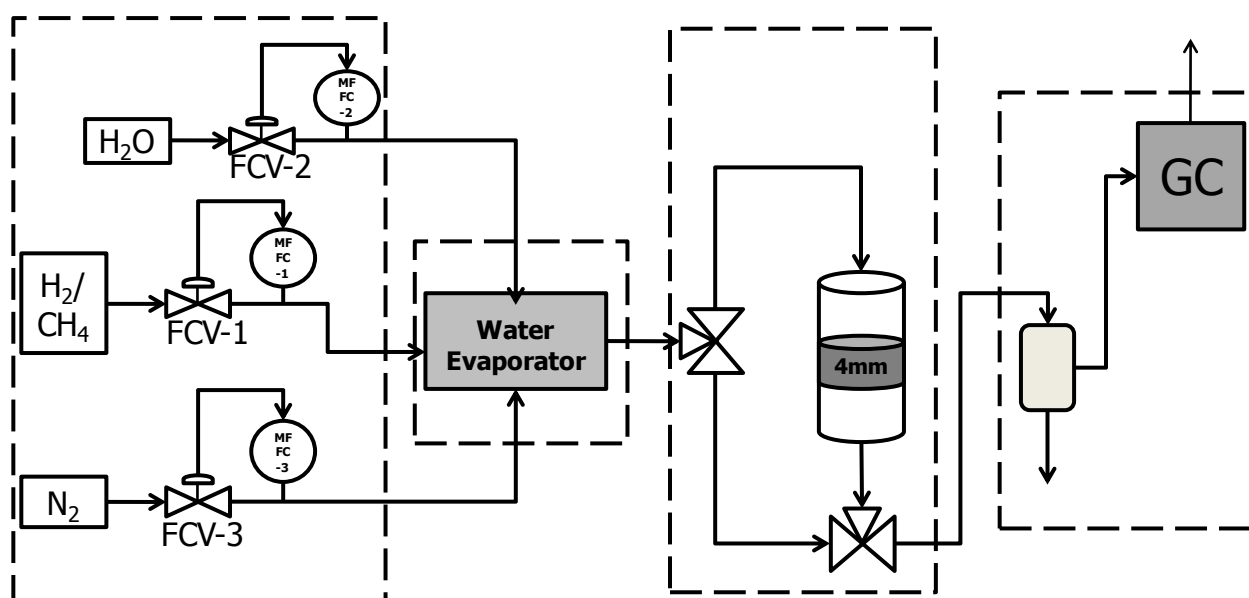


Figure 2.1: MSR Process Flowsheet Diagram

A feed section consists of an assembly of Bronkhorst mass flow controllers which are fed through 99.999% pure gases cylinders provided by SIAD. Ultrapure water obtained from a Millipore Milli-Q system with a resistivity $> 18 \text{ M}\Omega \text{ cm}^{-1}$ was used for preparing steam. The water was supplied through water tank operated with 4bar of compressed air and fed in the system through Bronkhorst flow controller. All the flow rates in the feed section were controlled by computer through Bronkhorst Flow DDE controller.

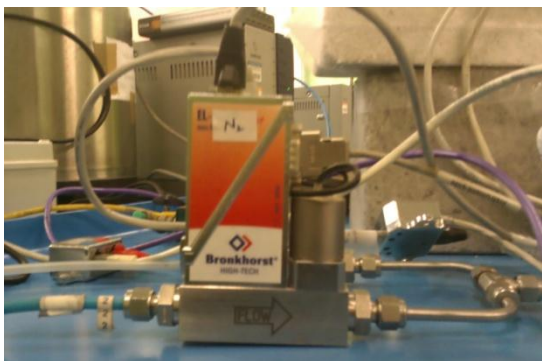


Figure 2.2: The feed section

A mixer/evaporator section after the feed section which serves dual purpose, first to evaporate the water and secondly to mix the gas stream with the steam generated within the system. The mixer/evaporator section operates at 130°C and is controlled by a West 6100+ heating system



Figure 2.3: Mixer Evaporator Section

A reactor/oven system following the mixer/evaporator section consists of a programmable heating furnace controlled by Lenton heater. The reactor consists of a 4mm ID quartz tube (in which 30mg of a catalyst diluted with 50mg of inert was placed between a quartz wool) inserted in the furnace. Provisions are made to bypass the reactor in order to increase the system flexibility. A water trap consisting of silica gel and condenser are placed at reactor outlet to condense the water in the system before entering an analysis section.



Figure 2.4: Reactor/Oven system

Finally the analysis section which consists of a gas chromatograph (Varian CP-3800) equipped with a thermal conductivity detector (TCD) and two Molsieve 5A columns.



Figure 2.5: Analysis section Varian CP-3800

2.2 Catalytic Activity

Catalytic activity tests on Steam Reforming (SR) of methane were conducted in a fixed-bed quartz micro-reactor with inner diameter of 4 mm at atmospheric pressure. Each sample (300 mg in powder, diluted with 500 mg of SiO₂ (0.2–0.7

mm) was placed between two quartz wool plugs in the centre of the quartz tube and inserted into the furnace heated to the reaction temperature. A K-type thermocouple was inserted into the reactor to measure temperature of catalytic bed. Before experiments, each catalyst was reduced with a mixture of 50% H₂ in N₂ by heating from room temperature to 200 °C, and by maintaining that temperature for 1 h. For SR process, the fixed bed was fed with an overall flow of 100 NmL min⁻¹, maintaining a steam-to-carbon ratio equal to 4, with a weight space velocity (WHSV) of 0.33 NL min⁻¹ g_{cat}⁻¹. The reaction temperature was varied from 400 to 750°C. The outlet gas stream was analyzed, after the removal of the water, through a gas chromatograph (Varian CP-3800) equipped with a thermal conductivity detector (TCD) and two Molsieve 5A columns.

For the OSR tests instead, the oxygen was added to the feed with an oxygen-to-carbon (O/C) molar ratio equal to 0.65, under lightly exothermic conditions, being all other conditions the same of the SR process (S/C molar ratio of 3). Such an O/C value was chosen to optimize fuel conversion and hydrogen concentration.

For all the performed tests, repeated at least three times for assuring the repeatability of the measures, the carbon balance was respected within 5%. All the measures were performed after condensing the remaining water in reformat: the reported values refer, too, to dry gas composition.

2.3 Catalytic Stability

The stability test was conducted under cyclic condition with daily startup and shutdown process (DSS). The cycle consisted of startup, reaction and shutdown processes. During startup process under inert conditions (DSS_{inert}) the catalyst bed was heated from ambient temperature to the working temperature in N₂ flow. Once the catalyst achieved the working temperature the N₂ flow was stopped and the reaction mixture flow was started. After 6 h of reaction time the heating and reaction mixture flow was stopped and the catalyst bed was cooled down to ambient temperature in N₂ flow.

During startup process under reaction conditions (DSS_{rxn}) the catalyst bed was heated from ambient temperature to the working temperature in reaction

mixture. Once the catalyst achieved the working temperature the reaction time was noted. After 6 h of reaction time the heating and reaction mixture flow was stopped and the catalyst bed was cooled down to ambient temperature in reaction mixture flow. After completion of stability tests the catalytic performance was re-evaluated in temperature range of 400°C-700°C.

2.4 Intrinsic Kinetics

For the kinetics the catalyst was heated to the desired temperature and after reaching isothermal conditions S/C ratio was varied to see the effect of methane and steam partial pressure on methane conversion, keeping WHSV constant. After this another set of experiment was conducted keeping S/C ratio constant at 3 and changing the space velocity. No inert was used in the experiments and no hydrogen was added in the feed as there was no visible catalyst deactivation.

2.4.1 Simulation method

The thermodynamic equilibrium can be calculated by two methods, one by equilibrium constants, while other one by minimization of free energies reforming reaction. The method of minimizing Gibbs free energy is normally favored in fuel-reforming analysis in contrast with the equilibrium constant due to presence of solid carbon which is difficult to analyze.

In order to analyze the performance of catalyst, it was compared with the results calculated by the simulation software. The operating conditions maintained the same as of practical test. The reactor was Gibbs free energy by using Peng-Robinson property set. The reforming reactor was modeled by using library model RGibbs. The RGibbs reactor of the AspenPlusTM was selected to calculate the chemical equilibrium value of MSR reaction by minimizing the Gibbs free energy of all the species expected to participate in the equilibrium. For simplification, components were limited to CH₄, H₂, CO, and CO₂. The RGibbs model is preferred in fuel-reforming analysis. The inlet flow rate of methane was adjusted at 100 NmL min⁻¹, 138 NmL min⁻¹ correspond to 20 WHSV and 27.65 WHSV at steam to carbon ratio 3.0 with pressure at 1 bar. In another comparison, the methane flow rate was 100 NmL min⁻¹, but varying the steam to carbon ration of 2.8, 3.0 and

3.2. The reactor temperature ranged from 400 to 750 °C. A sensitivity analysis of CO towards CH₄ has also been conducted with regard to the effect of varying temperature. The H₂/CH₄ also conducted to see the extent of the reaction i.e. how much methane is converted into H₂.

2.5 Catalysts Characterization:

2.5.1 Brunauer, Emmet, Teller (B.E.T)

The specific surface areas (S_{BET}) of the catalysts was determined using the Brunauer, Emmet, Teller (BET) method within the relative pressure range of 0 to 1 on an ASAP 2020 M Micromeritics Instrument. Nitrogen adsorption isotherms were recorded at –196 °C. Prior to adsorption, approximately 50.0 mg of solid powder were placed in the cell and evacuated at 350 °C for 3 h under high vacuum.

2.5.2 CO Chemisorption

By using the ASAP 2020 M Micromeritics Instrument the chemisorption analysis was carried out, in order to evaluate the active metals dispersion on supports. H₂ saturation was firstly performed by flowing 20 Ncm³ min^{–1} of H₂ for 2 h at 350 °C and at the end and He flow rate of 20 Ncm³ min^{–1} for 1.5 h was fed to the apparatus increasing the temperature to 370 °C. Then, at room temperature, a mixture of 10% CO in He was injected in pulses of 500 Nµl each, till the fulfillment of constant outlet peaks. The amount of adsorbed gas was determined as difference between the total injected volume and the residual escaped one. The metal dispersion on the carrier surface was determined as follows:

$$D_{\%} = 100 \cdot S_f \cdot \frac{V_{ads} \cdot M_{me}}{V_g \cdot F_{me}} \quad (1)$$

considering a stoichiometric factor S_f equal to 1 (i.e., each Rh atom adsorbed one CO molecule), the total volume of CO chemisorbed referred to the mass of the carrier used for the analysis in Ncm³ g^{–1} (V_{ads}), the metal atomic weight M_{me} (101.07 g mol^{–1} for Ru; 102.91 g mol^{–1} for Rh; 195.08 g mol^{–1} for Pt,

respectively), the total mass fraction of the metal on the catalyst (F_{me} , expressed as $g_{me} g^{-1}$ of carrier) and that one gas g-mole, V_g , occupies 22,414 cm^3 at normal conditions.

2.5.3 X-ray diffraction (XRD)

The X-ray diffraction (XRD) patterns were collected using a Philips X-Pert MPD X-ray diffractometer equipped with a Cu K α radiation at 40 kV and 30 mA to verify the effective composition of the samples and derive qualitative indications of the presence of comparatively large noble metals crystallite from its eventually visible peaks. All powder samples were scanned over 2θ range between 20° to 70° over 1 h. The peaks were assigned according to the PCPDFWIN database. The particle size of carriers was determined by Scherrer's equation, assuming a Gaussian shape of the peaks.

2.5.4 SEM & TEM

The morphology and metal particle size distribution of catalysts were examined by transmission electron microscopy (TEM Philips CM12).

2.5.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were carried out on Fe–NX/C samples using a Physical Electronics PHI 5800 (USA) multi-technique ESCA system (with monochromatic Al-K α X-ray radiation). The survey and narrow spectra were obtained under identical conditions and a charging correction with reference to C 1s at 285 eV, during which the samples were placed in an ultrahigh vacuum chamber at 2×10^{-10} Torr. Multipak 9.0 software was used for obtaining semi-quantitative atomic percentage compositions.

2.5.6 Catalyst Density (ρ)

The catalyst density was measured by Ultrapyc 1200e analyzer.

2.5.7 Metal Loading (ICP)

The catalyst metal loading was measured by ICP technique using a Thermo Fisher Scientific ICP-MS.

Part I: Catalytic Activity & Performance

In first part of the thesis the catalytic activity and performance of different noble metal catalysts (Ru, Rh and Pt) was evaluated. Part I consists **Chapter 3**, **Chapter 4**, **Chapter 5** and **Chapter 6** dealing with the basic screening of these catalysts.

Chapter 3 deals with the screening of Rh catalyst over MgO, Niobic acid and Niobia support.

Chapter 4 deals with the performance of Perovskites towards MSR reaction

Chapter 5 deals with the screening of Ru catalyst over MgO, Niobic acid and Niobia support. The effect of Niobic acid and niobia support was also determined.

Chapter 6 finally deals with the comparison of steam reforming and oxidative reforming reactions over different noble metals (Rh, Ru, Pt) on CeO₂ and Al₂O₃ support

Chapter 3 Methane steam reforming over supported Rh catalyst

3.1 Introduction:

In order to explore highly active and selective catalysts for the MSR process, in this work comparative analysis of Rh catalysts on different supports was evaluated. The supports for Rh catalyst used were MgO, Niobic acid and Niobia. Ru/MgO catalytic system has been studied for ammonia synthesis but not been utilized for MSR reaction¹. However MgO has been studied for MSR as an additive on Ni/Al₂O₃ catalyst and it tends to improve the CO₂ selectivity of the process². The niobic acid support is known for its acidic nature and no studies regarding MSR reaction are found although the niobic acid is known to facilitates the reaction involving water^{2,3}. Niobia on the other hand has been an active support ethanol steam reforming but no studies involving MSR is available⁴⁻⁶, also niobia tend to show strong metal support interaction⁷⁻¹¹.

3.2 Experimental:

3.2.1 Catalyst Synthesis

Three type of supports were prepared. Firstly a support labeled as MgO was synthesized by using a simultaneous combustion synthesis technique¹² through Mg(NO₃)₃ × 6H₂O precursor followed by a 3h air calcination at 650°C. Secondly a Niobic acid (Nb₂O₅·nH₂O, type HY-340, water content ≈ 20 wt.%) was supplied by the Companhia Brasileira de Metalurgia e Mineração (CBMM, Brasil) and used as support labeled as Nb₂O₅ and a third niobia support was prepared by thermal treatment of Niobic acid at 500°C for 5h¹³, and labeled as Nb₂O₅ (500 °C). All the three supports were impregnated by incipient wetness impregnation method

using aqueous solution of a RhCl_3 to obtain a nominal 1.5 wt% of Rh as catalysts. All the impregnated samples were further divided into two groups, one group was used as catalyst without any further treatment while the other group was calcined at 400°C for 3h¹⁴. The list of all the synthesized catalysts along with preparation conditions are tabulated in **Table 3.1**.

Table 3.1: List of prepared catalysts along with preparation conditions

Catalyst	Support	$T_{c, \text{support}}$	$T_{c, \text{final catalyst}}$
Rh/MgO	MgO	650	400
Rh/Nb ₂ O ₅	Nb ₂ O ₅	-	-
Rh/Nb ₂ O ₅ (500°C)	Nb ₂ O ₅ (500°C)	500	-
Rh/Nb ₂ O ₅ (400°C)	Nb ₂ O ₅	-	400
Rh/Nb ₂ O ₅ (500-400°C)	Nb ₂ O ₅ (500°C)	500	400
$T_{c, \text{support}}$ = Calcination temperature of support (°C)			
$T_{c, \text{final catalyst}}$ = Calcination temperature after Rh impregnation (°C)			

3.2.2 Catalytic Activity

The catalytic activity of the catalyst was evaluated in temperature range of 400-750°C. Details of catalytic activity measurements are presented in **Chapter 2**

3.2.3 Catalysts Characterization:

The catalyst prepared were characterized by CO Chemisorption, XRD, SEM EDX and XPS analysis

3.3 Results and Discussion:

All of the prepared catalysts were tested towards the MSR reaction with a S/C ratio 4. The obtained results are shown in **Figure 3.1(A-C)**. At first a comparison of all the catalysts was made in terms of methane conversion, CO₂ selectivity and H₂ dry outlet concentration.

The Rh/MgO achieved 93% methane conversion at 650°C with a H₂ dry outlet concentration and a CO₂ selectivity of 78% and 63% respectively. Further

increase in the temperature to 700 and 750°C improved the methane conversion and the H₂ dry outlet concentration for Rh/MgO, however the CO₂ selectivity decreased to 51%.

For the Rh/MgO increase in the temperature to 700°C resulted in 98% methane conversion with a H₂ dry outlet concentration and a CO₂ selectivity of 78% and 51% respectively. Further increase of the temperature to 750°C had a small effect on methane conversion as it reached 99%; however the H₂ dry outlet concentration and the CO₂ selectivity remain similar.

The Rh/Nb₂O₅ showed an increase in methane conversion with the temperature increase till 650°C where it reached a maximum methane conversion of 86% with 78% CO₂ selectivity and 74% H₂ in dry reformat. These values at 650°C are lower than that obtained on the Rh/MgO. The increase in temperature, for Rh/Nb₂O₅ catalyst, to 700°C and 750°C resulted in decrease in the methane conversion to 81% and 80% respectively.

When the Rh/Nb₂O₅ was calcined at 400°C for 3h we obtained the Rh/Nb₂O₅(400°C) catalyst. This calcinations at 400°C improved the catalytic activity of Rh/Nb₂O₅(400°C) as presented in **Figure 3.1**. On the other hand the influence of calcinations on Rh/Nb₂O₅(400°C) in terms of the methane conversion and H₂ dry outlet concentration was negligible as the values obtained were more or less similar to Rh/Nb₂O₅. However for CO₂ selectivity a slight decrease was observed as the Rh/Nb₂O₅(400°C) achieved 73% and 67% CO₂ selectivity at 700°C and 750°C respectively.

The support calcinations effect was not visible for the Rh/Nb₂O₅(500°C) regarding the methane conversion as it reached a maximum of 88% at 700°C and remained constant at 750°C lower than Rh/Nb₂O₅ catalyst. However, for the H₂ dry outlet concentration the Rh/Nb₂O₅(500°C) showed 74% at 700°C but at 750°C the H₂ dry outlet concentration increased to 75%. The CO₂ selectivity remained lower for Rh/Nb₂O₅(500°C) and could only achieve 72% at 750°C.

When the Rh/Nb₂O₅(500°C) was calcined at 400°C for 3h we obtained the Rh/Nb₂O₅(500°C-400°C) catalyst. The catalytic activity in terms of the methane

conversion and the H₂ dry outlet concentration for Rh/Nb₂O₅ catalyst reached 89% methane conversion with 74% H₂ in dry outlet concentration at 650°C. The temperature increase to 750 °C improved the methane conversion to 93%. However, the H₂ in dry outlet concentration slightly increased to 75%.

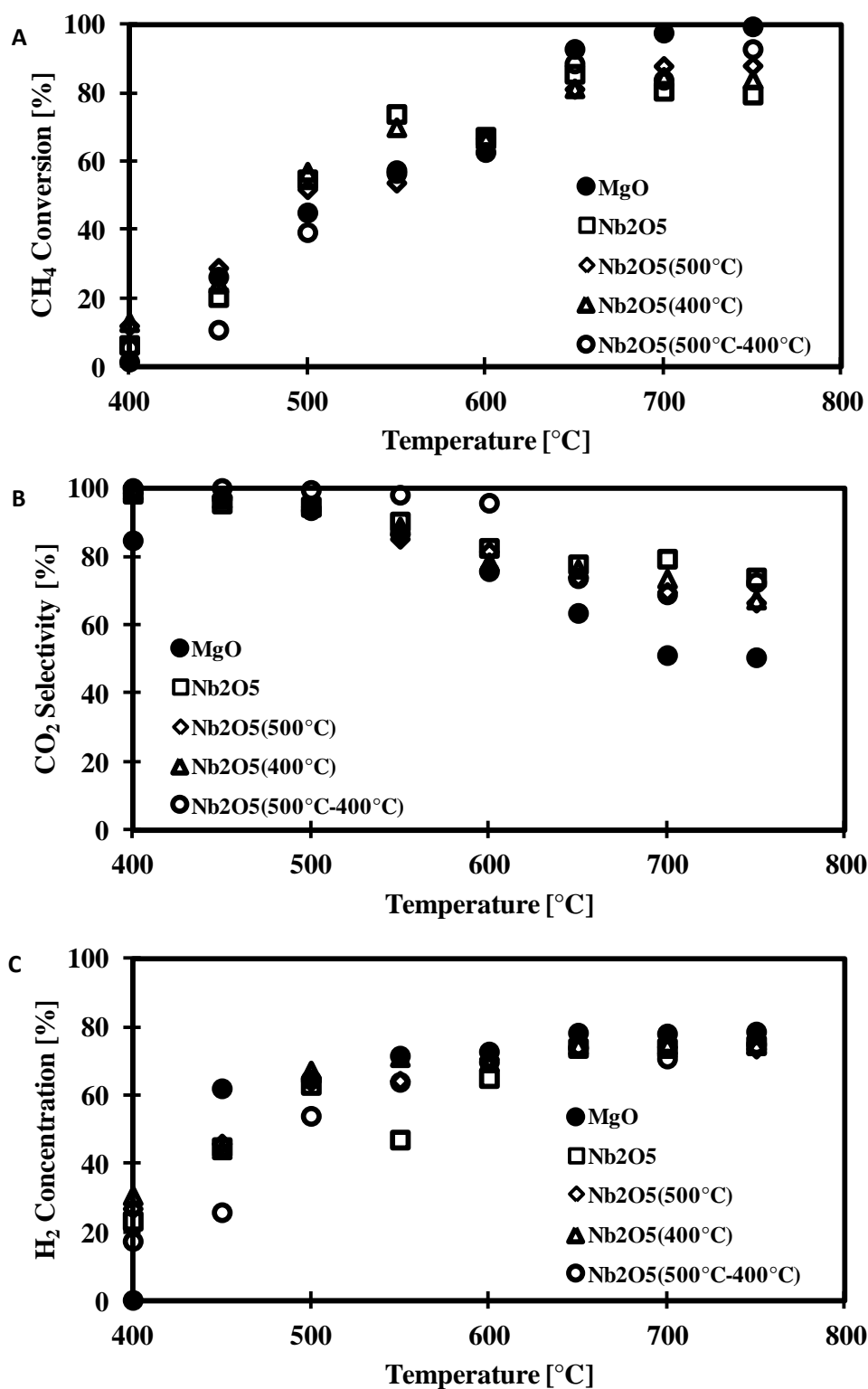


Figure 3.1: Methane Conversion (A), CO₂ selectivity (B) and H₂ dry outlet concentration (C) of all the prepared catalysts

Summarizing, among these five catalysts tested towards MSR reaction only two [Rh/MgO, Rh/Nb₂O₅(500°C-400°C)] reached above 90% methane conversion at

750°C, while with the other three catalysts [Rh/Nb₂O₅, Rh/Nb₂O₅(500°C), Rh/Nb₂O₅(400°C)] showed less than 90% conversion at 750°C.

The activity of these catalysts is comparable to other catalysts available in literature as these are highly active at lower temperatures^{15–19}. The activity of the Rh/MgO can be attributed to the effect caused by the MgO support which enhances CO₂ selectivity and H₂ production^{2,20}. The Niobic acid supported catalysts showed excellent catalytic activity and niobia supported catalysts were also good for methane steam reforming. Overall the niobic acid and niobia supported Rh catalysts showed high CO₂ selectivity. This higher selectivity of Rh and niobic acid and niobia support can be associated with the strong metal support interaction⁹. The niobia supported catalysts showed activity better than ethanol steam reforming reaction^{21,22}. All these Rh catalysts were equally active for water gas shift reaction as reaction resulted in high CO₂ selectivity²³.

As the catalysts were active at 650 to 750°C resulting in above 80% methane conversion, to further observe the extent of water gas shift reaction the catalysts were compared for a CO₂/CO selectivity ratio ($S_{\text{CO}_2/\text{CO}}$), a H₂-to-CO molar ratio (H₂/CO) and a hydrogen-to-methane reacted molar ratio (H₂/CH_{4,reacted}) and the subsequent values are presented in **Table 3.2**. In general, the water gas shift activity decreased by temperature increment, as the $S_{\text{CO}_2/\text{CO}}$ and H₂/CO values decreased for all the catalysts by increasing the temperature from 650 to 750°C. For the Rh/MgO at temperature increment from 700°C to 750°C, $S_{\text{CO}_2/\text{CO}}$ and H₂/CO remained constant at 1 and 7.5 respectively. Concerning the Rh/Nb₂O₅ catalyst temperature increment decreased the $S_{\text{CO}_2/\text{CO}}$ and H₂/CO from 3.8 and 17 at 700°C to 2.8 and 14 at 750°C respectively. All these catalysts showed a selectivity ratio higher than 1 indicating the presence of water gas shift reaction and higher H₂/CO molar ratio compared to available in literature^{15,17}. A very slight change in H₂/CH_{4,reacted} was observed for all the catalysts from 650°C to 750°C temperature increment and the Rh/MgO showed the highest value for H₂/CH_{4,reacted}.

Table 3.2: Selectivity and molar ratios of the best performing catalysts

Catalyst	T(°C)	S _{CO₂/CO}	H ₂ /CO	H ₂ /CH _{4,reacted}
Rh/MgO	650	1.74	10.7	3.9
	700	1.05	7.5	3.7
	750	1.02	7.5	3.7
Rh/Nb₂O₅	650	3.5	15	3.3
	700	3.8	17	3.5
	750	2.8	14	3.7
Rh/Nb₂O₅(500°C)	650	2.8	13	3.5
	700	2.3	11	3.3
	750	2.0	9	3.2
Rh/Nb₂O₅(400°C)	650	3.2	15	3.6
	700	2.8	13	3.5
	750	2.1	11	3.5
Rh/Nb₂O₅(500°C-400°C)	650	2.8	12	3.2
	700	2.2	9	2.9
	750	2.6	12	3.2

3.3.1 Rh/MgO Characteristics:

As Rh/MgO achieved 99% methane conversion, physical characterization of the catalyst was performed. **Table 3.3** depicts the physical characteristics of the catalyst.

Table 3.3: Physical characteristics of the best performing catalysts CO Chemisorption Analysis

Catalyst	Rh (wt%)	D (%)	Crystallite Size (nm)
Rh/MgO	1.5	13.3	8.2
Rh/Nb ₂ O ₅	1.5	4.7	23.3
Rh/Nb ₂ O ₅ (500°C)	1.5	12.8	8.5

The XRD analysis of the catalyst is shown in **Figure 3.2** .

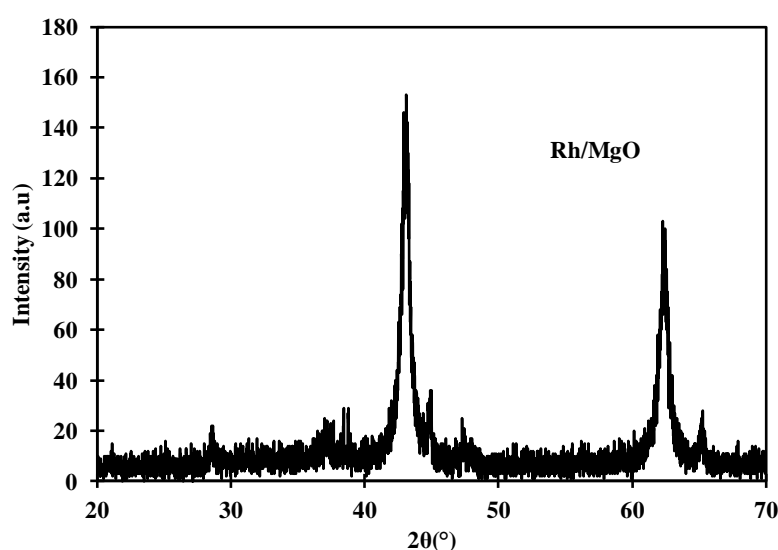


Figure 3.2: XRD Pattern of Rh/MgO

The catalyst showed a crystalline structure. For the peaks related to magnesia periclase phase the Rh/MgO catalyst showed peaks at $2\theta = 43.11^\circ$, and 62.31° . A slight shift of these peaks to higher degree compared to pure periclase (01-071-1176, $2\theta = 36.88^\circ$, 42.85° , and 62.21°) can be envisaged. No peaks related to Rh are visible on Rh/MgO.

The FESEM micrograph of the Rh/MgO catalyst is presented in **Figure 3.3**. A blend of crystalline and porous surface morphology was observed for the Rh/MgO. At 10 μm magnification **Figure 3.3-A** a mixed crystalline and

amorphous structure is visible, however at 1 μm magnification **Figure 3.3-B** only porous structure is visible.

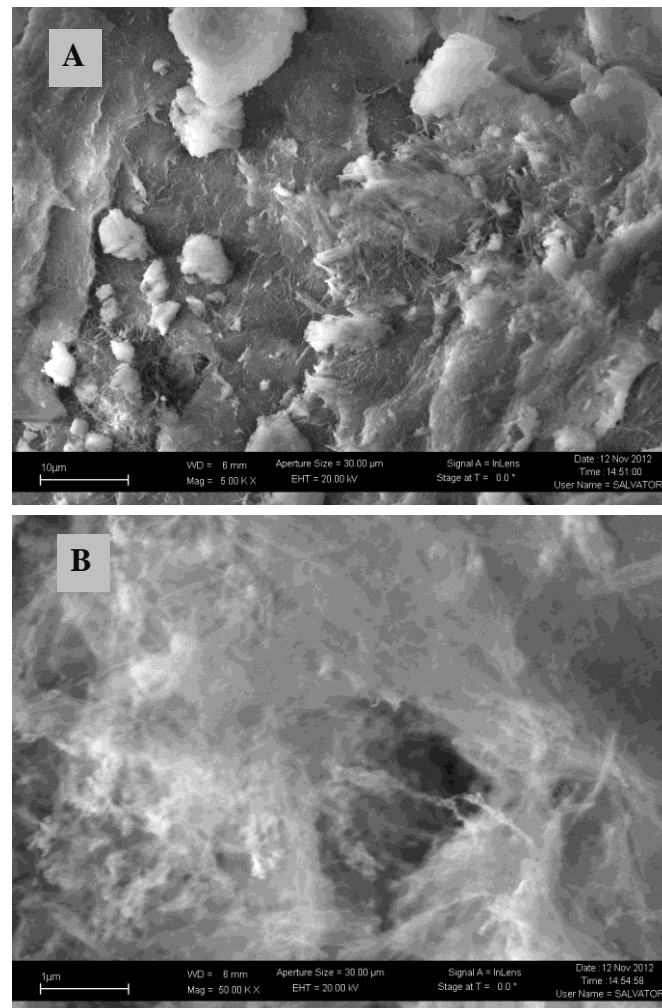


Figure 3.3: FESEM micrograph of as prepared Rh/MgO

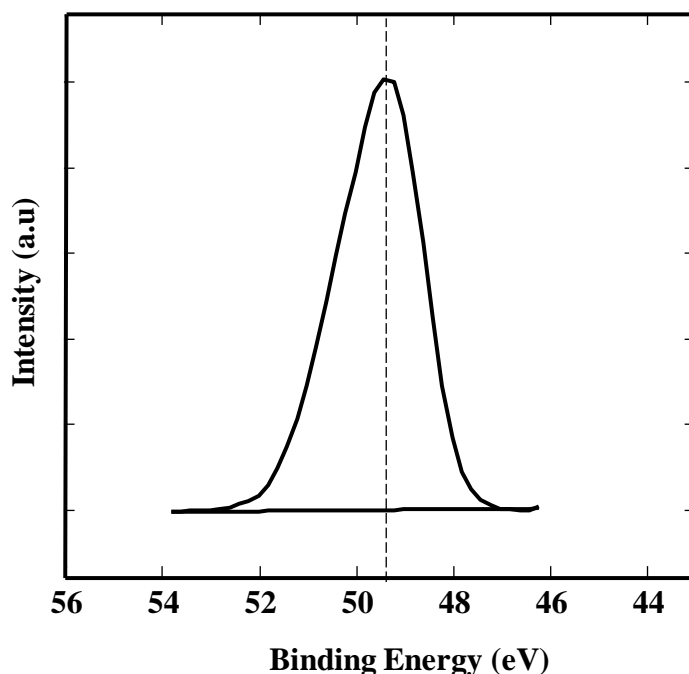


Figure 3.4: Mg 2p binding energy spectrum

Figure 3.4 shows a binding energy spectrum of Mg 2p for the Rh/MgO catalyst and the surface atomic percentage and binding energy values are presented in **Table 3.4**. Rh/MgO showed only one peak of Mg 2p with a binding energy value 49.56 eV. These binding energy values are slightly lower than that of bulk Mg 2p value of 49.6 eV²⁴. This slightly negative shift of binding energy indicates that the Mg is present in Mg²⁺ state^{25,26} mainly due to hygroscopic nature of magnesia¹

Table 3.4: XPS analysis of the catalysts

Catalyst	Atomic (%) XPS			Atomic Ratio XPS Rh/Support	Mg 2p
	O	Rh	Nb or Mg		
Rh/MgO	81.7	0.1	0.1	1	49.56
Rh/ Nb ₂ O ₅	53.0	0.4	22.6	0.018	
Ru_n/ Nb ₂ O ₅ (500°C)	52.9	1	21.9	0.046	

3.3.2 Effect of Niobic acid and Niobia Support:

To compare the effect of Niobic acid and niobia support on Rh catalyst, the physical characteristics of the two supports are compared in **Table 3.3**. The

Nb_2O_5 showed less metallic dispersion and large crystallite size than $\text{Nb}_2\text{O}_5(500^\circ\text{C})$, so the observed catalytic activity difference of two supports can be associated with the difference in metallic dispersion.

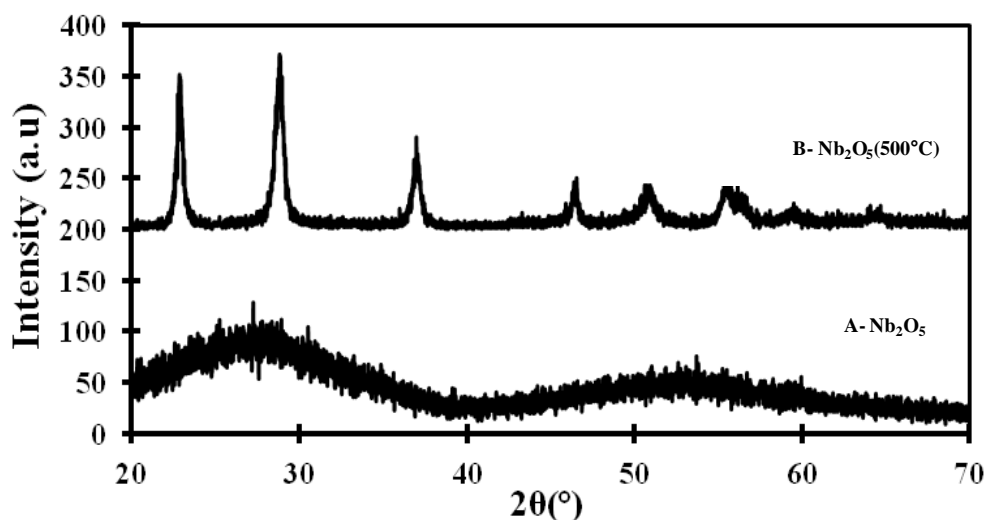


Figure 3.5: XRD diffractogram of (A) Niobic acid, (B) Niobia supported Rh. XRD diffractogram of the two catalysts is presented in **Figure 3.5**. It is clear that the $\text{Rh}/\text{Nb}_2\text{O}_5$ show an amorphous structure related to niobic acid (HY-340)^{13,27}. On the other hand the $\text{Rh}/\text{Nb}_2\text{O}_5(500^\circ\text{C})$ showed peaks at $2\theta = 22.60^\circ, 28.56^\circ, 36.73^\circ, 46.23^\circ, 50.65^\circ$ and 55.24° , related to crystalline tetragonal phase of Nb_2O_5 ¹³. The absence of Rh related peaks on the $\text{Rh}/\text{Nb}_2\text{O}_5(500^\circ\text{C})$ can be due to fine dispersion of Rh in oxide form over the support.

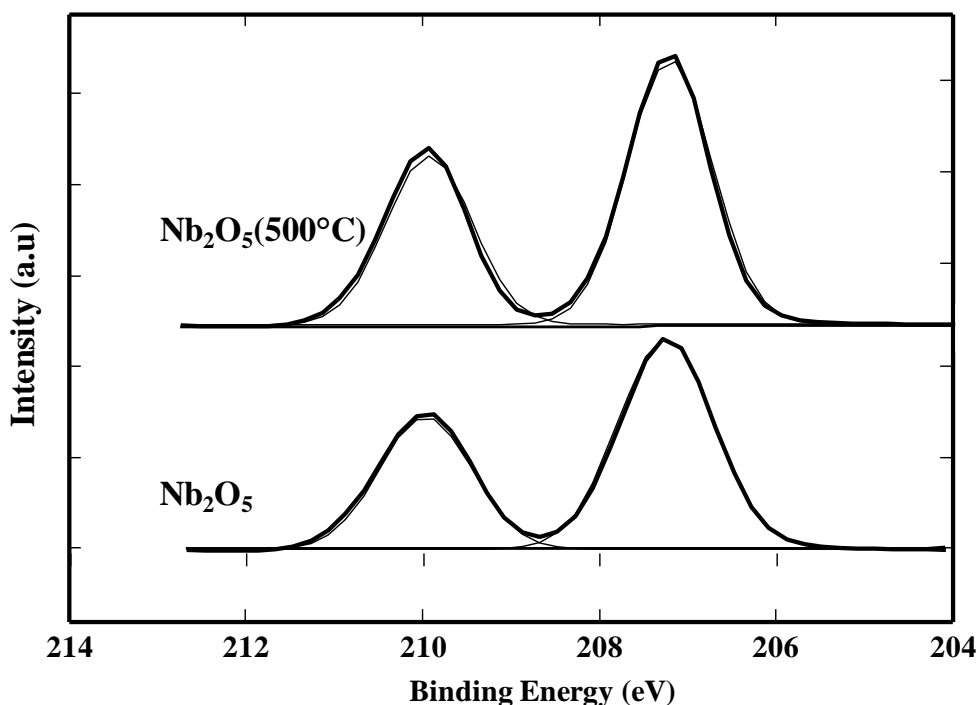


Figure 3.6: Nb 3d binding energy spectrum

The typical XPS spectrum of Nb 3d is shown in **Figure 3.6** and binding energy values are tabulated in **Table 3.5**. From **Table 3.5** the Rh/Nb₂O₅ shows the 3d_{5/2} binding energy value of 207.23 eV while the Rh/Nb₂O₅(500°C) showed a value of 207.221 eV. The value of Nb 3d_{5/2} binding energy depicted by the catalysts is associated to bulk Nb where 3d_{5/2} binding energy is observed at 207.5 eV^{28,29}. The analysis of Nb 3d_{3/2} binding energy shows the value of 209.96 eV and 209.93 eV for Rh/Nb₂O₅ and Rh/Nb₂O₅(500°C) respectively. The XPS results indicate that the surface composition and the state of support is the same for both niobic acid and niobia respectively. So the change in catalytic activity depends mainly on the metallic dispersion of the catalyst.

Table 3.5: Binding energies of Niobic acid and niobia support

Catalyst	Nb 3d			
	3d _{5/2}	%	3d _{3/2}	%
Rh/ Nb ₂ O ₅	207.23	60.70	209.96	39.30
Ru_n/ Nb ₂ O ₅ (500°C)	207.21	60.67	209.93	39.33

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Chapter 4 Methane steam reforming over Perovskites

4.1 Introduction:

The carbon deposition on the catalyst during MSR reaction is a problem which can be resolved by replacing the conventional unreactive supports. The conventional support like Al_2O_3 can be replaced with supports which provide lattice oxygen. The lattice oxygen reacts with the deposited carbon thus minimizing the carbon deposition.

Supports like CeO_2 have been widely studied for their ability to provide lattice oxygen. Apart from CeO_2 , perovskites are also structurally capable of providing with the lattice oxygen which enhances the steam reforming reaction. Perovskites have been studied for steam reforming reactions of ethanol^{1,2} and methane³⁻⁶. Also dry reforming studies have been made on perovskites⁷. Usually Ni based perovskites have been utilized for MSR reaction.

However, the activity of the perovskites depends mainly on the species within the perovskite structure and the interaction between the species. Also in some cases the operational characteristics like steam to carbon ratio play an important role in determining the catalytic activity of the perovskite. There are contradictory studies available in literature. For example Provendier et al.⁵ found LaNiFeO_3 catalyst more active at S/C ratio 1 than at S/C ratio 3. On contrary Urasaki et. al.² conducted steam reforming at S/C ratio 10 and found the perovskite structure active for reforming.

In this work the mixed perovskites were synthesized and tested towards MSR reaction. The effect of noble metal impregnation on the $\text{LaMn}_{0.7}\text{Cu}_{0.3}\text{O}_3$ perovskite was also evaluated.

4.2 Experimental:

4.2.1 Catalyst Synthesis

The polycrystalline samples of perovskites were prepared by a solid-state reaction and glycerin-nitrate technique. The list of all the prepared perovskite is presented as follows:

1. $\text{La}_{0.9}\text{Sr}_{0.1}\text{Mn}_{0.7}\text{Cu}_{0.3}\text{O}_3$
2. $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.9}\text{Cu}_{0.1}\text{O}_3$
3. $\text{LaMn}_{0.7}\text{Cu}_{0.3}\text{O}_3$
4. $\text{LaMn}_{0.9}\text{Cu}_{0.1}\text{O}_3$
5. $\text{SmBaCo}_2\text{O}_{5.5}$
6. $\text{SmBaCo}_{1.6}\text{Cu}_{0.4}\text{O}_{5.5}$
7. $\text{SmBaCo}_{1.6}\text{Ni}_{0.4}\text{O}_{5.5}$
8. $\text{SmBaCo}_{1.6}\text{Fe}_{0.4}\text{O}_{5.5}$

Rare earth oxides with the purity not less than 99.99%, barium carbonate BaCO_3 (special purity grade), 3d-transition metal oxides: Fe_2O_3 , Co_3O_4 , NiO and CuO (either pure for analysis or special purity grade) or metallic cobalt and iron oxalate $\text{FeC}_2\text{O}_4 \times 2\text{H}_2\text{O}$ (pure for analysis grade), nitric acid and glycerin both of pure for analysis grade were used as starting materials. According to the solid state route initial oxides and barium carbonate were mixed in appropriate ratios, grinded in the agate mortar in alcohol media and fired by stages within the temperature range 850-1100 °C. According to the glycerin-nitrate technique rare earth oxides, barium carbonate, metallic cobalt and iron oxalate or Ni or Cu oxides were dissolved in the 4.5M nitric acid while heating, then glycerin was added in amount equivalent to a complete reduction of nitrate groups. Then solution was dried to a viscous gel that further transformed to a brown powder. In both methods final anneals were performed at 950-1100 °C in air with intermediate grindings during 100-120 h with following slow cooling to room temperature at the rate of about 100 °C/h

4.2.2 Catalytic Activity

The catalytic activity of the catalyst was evaluated in temperature range of 400-750°C. Details of catalytic activity measurements are presented in **Chapter 2**

4.3 Results and Discussion:

All the prepared catalysts were tested towards the MSR reaction with a S/C ratio 4. At first a comparison of all the catalysts was made in terms of methane conversion as shown in **Figure 4.1**

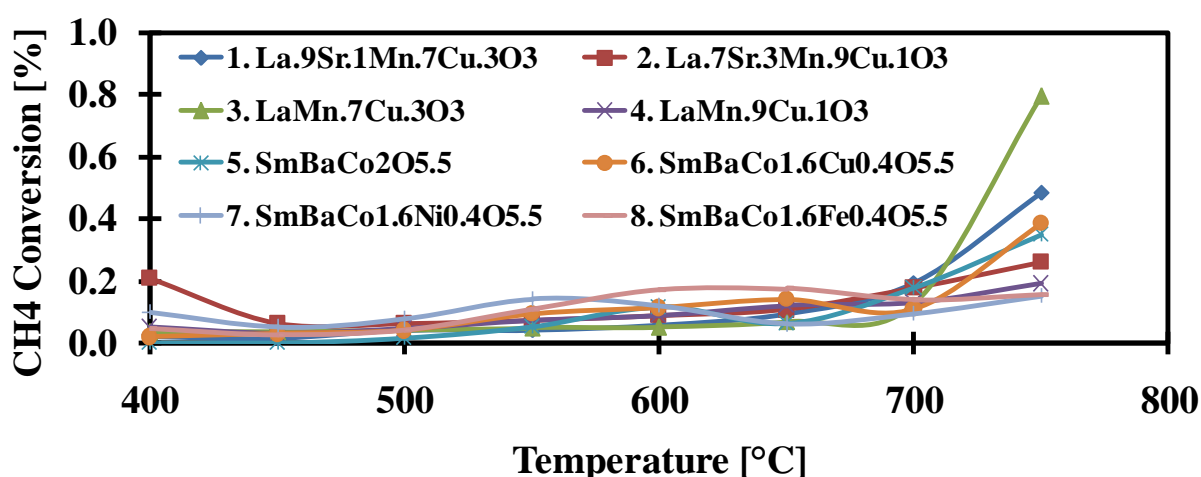


Figure 4.1: Methane conversion for all the prepared catalysts

From **Figure 4.1** the observed methane conversion for the perovskites remained lower than 1%. Only LaMn_{0.7}Cu_{0.3}O₃ could reach a conversion as high as 0.79%. All the other catalysts showed conversion below 0.5%. The resulted low conversion can be due to the structural changes within the catalyst due to reduction of the perovskite before the reaction⁷. Also for La perovskite the high S/C ratio enhances the oxidizing power of the catalyst therefore resulting in decrease of catalytic activity⁵.

To see the effect of perovskite as support in MSR reaction 1.5% Rh was deposited on LaMn_{0.7}Cu_{0.3}O₃ by incipient wetness impregnation method and calcined at 400°C for 3h. **Figure 4.2** shows the MSR activity of Rh/LaMn_{0.7}Cu_{0.3}O₃ catalyst in terms of methane conversion. The catalytic activity improved as the catalyst achieved 72% methane conversion at 750°C. The

methane conversion is lower compared to other supported noble metal catalysts available in literature.

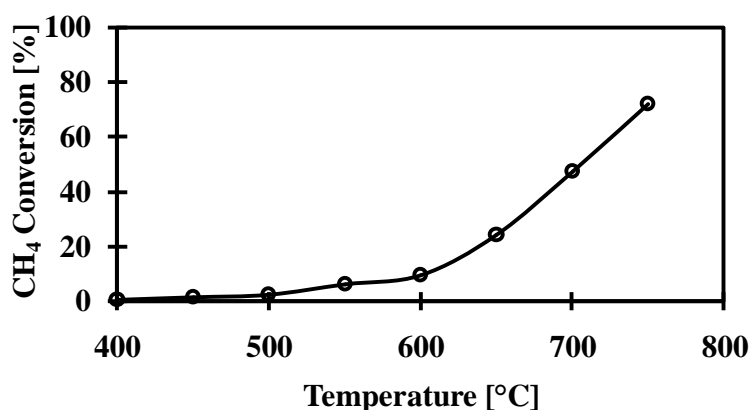


Figure 4.2: Methane conversion for Rh/LaMn_{0.7}Cu_{0.3}O₃

To observe the effectiveness of MSR reaction on the Rh/LaMn_{0.7}Cu_{0.3}O₃ catalyst, the H₂ dry outlet concentration and CO₂ selectivity are shown in **Figure 4.3**. The catalyst could only achieve 65% H₂ dry outlet concentration with 45% CO₂ selectivity.

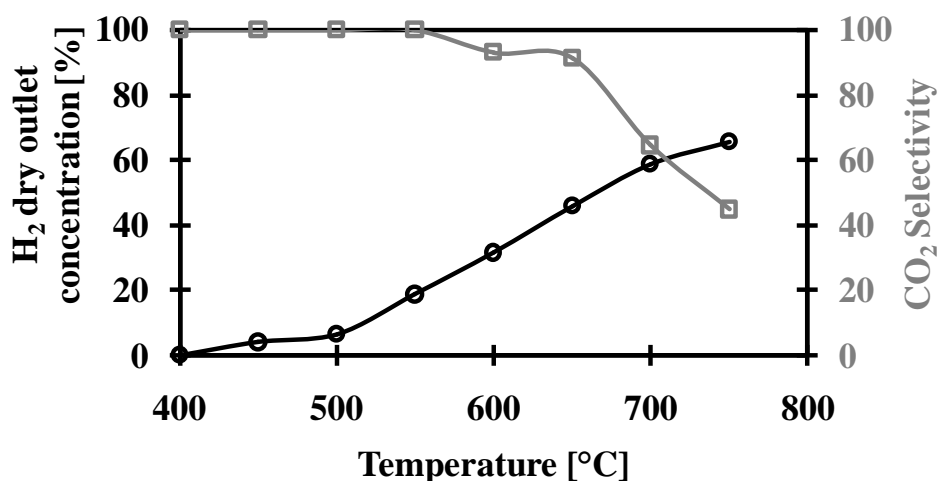


Figure 4.3: H₂ dry outlet concentration (black line and symbol) and CO₂ selectivity (gray line and symbol) for Rh/LaMn_{0.7}Cu_{0.3}O₃

4.4 References

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Chapter 5 : Methane steam reforming over supported Ru catalyst: Effect of Support and Calcination Temperature.

5.1 Introduction

Hydrogen has to face many challenges from current commercial scale to future fuel for fuel cells (FCs). Due to absence of hydrogen delivery and storage system, the primary challenge in this context is the hydrogen production directly on board vehicles or on stationary mode using fuel processors^{1,2}. Commercially hydrogen is produced alongside CO and CO₂ through catalytic MSR process usually with a steam to carbon ratio (S/C) of 2 to 5, over Ni catalyst at 1100°C³⁻⁵. The catalytic MSR process is preferred among other catalytic processes like partial oxidation and auto thermal reforming due to its high efficiency, lower emissions and lower cost^{6,7}.

When hydrogen is produced from MSR processes, the product obtained is the syngas, which must be cleaned up to remove CO for obtaining a hydrogen-rich gas stream. CO, in fact, acts as a poison for FCs. When the catalytic MSR process is squeezed to small scale due to space shortage for on-board production, a problem of CO separation from hydrogen arises⁵⁻¹⁰. Thus, research focused the attention to develop catalysts which produces minimum CO content without affecting hydrogen production. Nickel-based catalysts are effective industrially, but due to high metal loading, higher operating temperatures and carbon whiskers formation, attention is being focused on noble metal catalysts which operate at much lower temperatures, with low metallic loading and minimum carbon formation¹¹⁻¹⁴.

The present manuscript shows a comparative analysis of Ru-based catalysts on different supports to identify highly active and selective catalysts for the MSR process. Magnesia (MgO), niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) and niobia, or niobium pentoxide (Nb_2O_5), were used as support for Ru. Ru/MgO catalyst has been studied for ammonia synthesis¹⁵ but not for MSR reaction. However, MgO has been employed as an additive on Ni/ Al_2O_3 catalyst for MSR: it improved the CO_2 selectivity of the process¹⁶. The niobic acid is known for its acidic nature and no studies regarding MSR reaction are available. The niobic acid is known to facilitates the reaction involving water^{16,17}, while niobia provides strong metal-carrier interaction^{18–22}. Niobia on the other hand has been employed as an active support for ethanol steam reforming^{23–25}, but studies involving MSR are unavailable.

5.2 Materials and methods

5.2.1 Chemicals

Magnesium(III) nitrate hexahydrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.999% purity), urea NH_2CONH_2 ($\geq 98\%$ purity), ruthenium(III) chloride hydrate $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (99.9% purity, degree of hydration, ≤ 1), and ruthenium(III) nitrosyl nitrate $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (Ru 1.5%, in dilute nitric acid) were purchase from Sigma Aldrich. Niobic acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, type HY-340, water content ≈ 20 wt.%) was supplied by the Companhia Brasileira de Metalurgia e Mineração (CBMM, Brasil). Ultrapure water obtained from a Millipore Milli-Q system with a resistivity $> 18 \text{ M}\Omega \text{ cm}^{-1}$ was used for preparing aqueous solutions and steam. Pure methane (99.999%), hydrogen (99.999%) and nitrogen (99.999%) gases were supplied in cylinders provided by SIAD and used as received.

5.2.2 Preparation of the catalysts

Three type of carriers were prepared. MgO was synthesized by using a simultaneous combustion synthesis technique^{11,26} with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and urea at 350°C , followed by a 3h calcination at 650°C in static air. Niobic acid was used to prepare Nb_2O_5 in two different ways:

- as received (hereafter labeled as Nb₂O₅);
- washed with deionized water four times, dried at 90 °C for 72 h and calcined in furnace at 500 °C for 5 h in static air (hereafter labeled as Nb₂O₅_500)^{24,27}.

The three supports (MgO, Nb₂O₅, and Nb₂O₅_500) were impregnated with Ru by incipient wetness impregnation (IWI) method using aqueous solution of a Ru(NO)(NO₃)₃ or RuCl₃ to obtain a nominal 1.5 wt% of Ru as active element. An aqueous solution of the metal precursor was prepared and deposited drop by drop on the carrier, meanwhile thoroughly mixing the whole mass at about 130 °C in order to let the water evaporate together with N₂. The samples obtained were labeled as Ru_n/support and Ru_c/support, respectively. All of the impregnated samples were further divided into two groups: the first group was used as catalyst without any further calcination treatment while the second group was calcined at 400 °C for 3 h in calm air²⁸. The list of all of the synthesized catalysts along with the various preparation conditions is tabulated in **Table 5.1**.

Table 5.1: List of the 1.5 nominal wt.% Ru catalysts prepared along with preparation conditions ($T_{C,support}$ = calcination temperature of the support; $T_{C,catalyst}$ = calcination temperature of the catalyst after Ru impregnation), and physical characterization of the best performing ones (n.d.: not determined). Ru loading determined by EDX analysis.

Catalyst	Support	$T_{C,support}$ [°C]	$T_{C,catalyst}$ [°C]	Ru loading [%at.]	S_{BET} [m ² g ⁻¹]	D [%]	Crystallite size [nm]
Ru_c/MgO	MgO	650	400	2.2	15.7	3.4	38.4
Ru_n/MgO	MgO	650	400	2.4	6.7	44.7	2.9
Ru_c/Nb ₂ O ₅	Nb ₂ O ₅	-	-	3.0	98.7	5.8	22.8

Ru_n/Nb ₂ O ₅	Nb ₂ O ₅	-	-	1.9	114.7	86.1	1.5
Ru_c_400/Nb ₂ O ₅	Nb ₂ O ₅	-	400	0.8	67.9	12.2	10.8
Ru_n_400/Nb ₂ O ₅	Nb ₂ O ₅	-	400	n.d.	n.d.	n.d.	n.d.
Ru_c/Nb ₂ O ₅ _500	Nb ₂ O ₅	500	-	n.d.	n.d.	n.d.	n.d.
Ru_n/Nb ₂ O ₅ _500	Nb ₂ O ₅	500	-	1.5	43.3	< 1%	n.d.
Ru_c_400/Nb ₂ O ₅ _500	Nb ₂ O ₅	500	400	n.d.	n.d.	n.d.	n.d.
Ru_n_400/Nb ₂ O ₅ _500	Nb ₂ O ₅	500	400	n.d.	n.d.	n.d.	n.d.

5.2.3 Catalytic Activity

The catalytic activity of the catalyst was evaluated in temperature range of 400-750°C. Details of catalytic activity measurements are presented in **Chapter 2**

5.2.4 Catalysts Characterization:

The catalyst prepared were characterized by BET, CO Chemisorption, XRD, SEM EDX and XPS analysis

5.3 Results and Discussion

All of the prepared catalysts were tested towards the MSR reaction, with a S/C ratio equal to 4, in terms of CH₄ conversion, CO₂ selectivity, and H₂ dry outlet concentration, and their performance compared (**Figure 5.1**).

At 650 °C the Ru_n/MgO and the Ru_c/MgO catalysts (**Figure 5.1a,b**) showed similar performance by achieving CH₄ conversion higher than 91%, with CO₂ selectivity and H₂ dry outlet concentration above 68% and 70%, respectively. An increase of the temperature to 750°C improved the CH₄, (99% for Ru_n/MgO and 98% for Ru_c/MgO), the H₂ dry outlet concentration (78% for Ru_n/MgO and 71% for Ru_c/MgO), while the CO₂ selectivity slightly decreased (62% for Ru_n/MgO and 55% for Ru_c/MgO).

The Ru-based catalysts obtained by Ru deposition on thermally untreated Nb₂O₅ (**Figure 5.1c,d**) performed slightly better compared to the MgO-based catalysts in the range 650-750 °C. The best performance belongs to the Ru_c/Nb₂O₅ catalysts with full CH₄ conversion, 71% selectivity, and 78% H₂ dry outlet concentration.

The calcination treatment at 400 °C for 3h on the Ru-based catalysts on thermally untreated Nb₂O₅ after the IWI process (**Figure 5.1e,f**) worsened the performance of the Ru_c_400/Nb₂O₅, and in a lesser extent the performance of the Ru_n_400/Nb₂O₅. In particular, the Ru_c_400/Nb₂O₅, reached 82% as maximum CH₄ conversion at 650 °C, then it decreased at higher temperature. The CO₂ selectivity and H₂ dry concentration were lower compared to the values of the previous catalysts.

The calcination treatment at 500 °C for 3 h only on the Nb₂O₅ carrier (**Figure 5.1g,h**) again affected the performance of both the Ru_n/Nb₂O₅_500 and the Ru_c/Nb₂O₅_500: none of them was able to reach full CH₄ conversion. Similarly to the Ru_c_400/Nb₂O₅, the Ru_n/Nb₂O₅_500 reached 80% as maximum CH₄ conversion, then it decreased at higher temperature. The CO₂ selectivity and H₂ dry concentration were lower compared to the values of the previous catalysts.

The double calcination treatment, at 500 °C on the Nb₂O₅ carrier, then at 400 °C for 3 h after the Ru deposition by IWI (**Figure 5.1i,j**) greatly affected the performance of the Ru_n_400/Nb₂O₅_500 and the Ru_c_400/Nb₂O₅_500 catalysts. They reach a maximum of 79% and 60% CH₄ conversion at 750 °C, respectively.

Summarizing, among all of the catalysts prepared, the calcination treatment on the support, or on the Ru-impregnated catalysts greatly affected the overall performance towards the MSR. Only six catalysts reached full CH₄ conversion between 700 and 750 °C (Ru_c/MgO, Ru_n/MgO, Ru_c/Nb₂O₅, Ru_n/Nb₂O₅, Ru_n/Nb₂O₅_500, and Ru_c_400/Nb₂O₅, respectively), while the other four showed less than 80% CH₄ conversion between 700 and 750 °C.

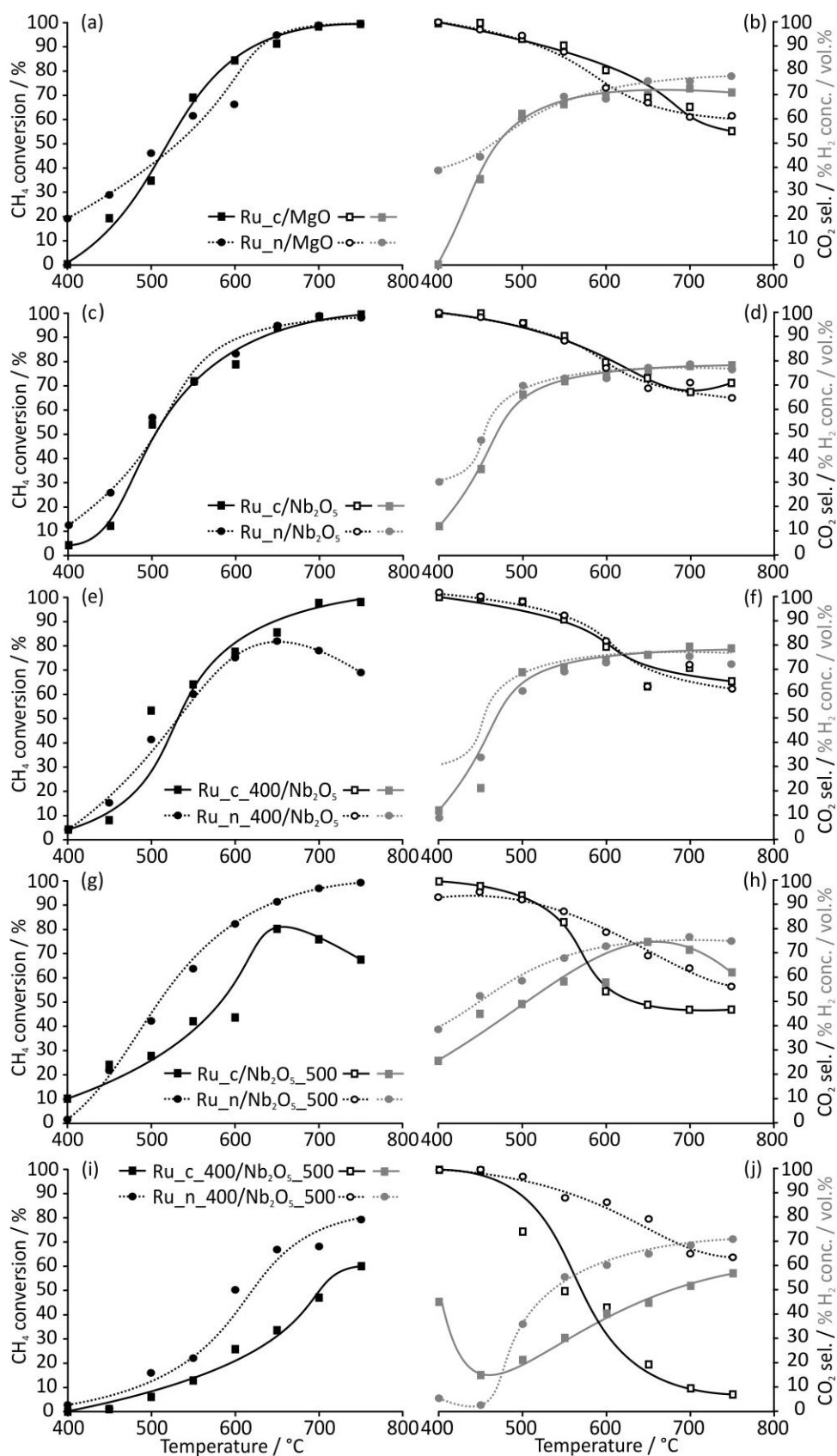


Figure 5.1: CH₄ conversion (full black symbols), CO₂ selectivity (empty black symbols), and H₂ dry outlet concentration (full gray symbols) for all of the catalysts prepared, as reported in Table 1 (a,b:MgO; c,d: Nb₂O₅, e,f:_400/Nb₂O₅,

g,h: Nb₂O₅_500;i,j:_400/Nb₂O₅_500; square symbols: Ru_c; circle symbols: Ru_n).

The best performing catalysts were selected for further investigations. Their activity is comparable to other Ru-based catalysts available in literature^{29–33}. The activity of the Ru_c/MgO and the Ru_n/MgO can be attributed to the effect caused by the MgO support which enhances CO₂ selectivity and H₂ production^{16,34}. The Nb₂O₅-supported catalysts and the Ru_n/Nb₂O₅_500 showed excellent catalytic activity towards the MSR, better than the ethanol steam reforming reaction^{35,36}. According to the literature³⁷ Ru-based catalysts are equally active for the water gas shift (WGS) reaction as reaction, too, assuring high CO₂ selectivity.

As the best performing catalysts were equally active between 700 and 750°C (CH₄ conversion between 97 and 100%), to further observe the extent of the WGS reaction these catalysts were compared in terms of CO₂-to-CO selectivity ratio ($S_{CO_2/CO}$), H₂-to-CO molar ratio (H₂/CO), and H₂-to-reacted CH₄ reacted molar ratio (H₂/CH_{4,reacted}), as tabulated in **Table 5.2**.

Table 5.2: Selectivity and molar ratios of the best performing catalysts at 700 and 750 °C

Catalyst	Reaction T [°C]	$S_{CO_2/CO}$	H ₂ /CO	H ₂ /CH _{4,reacted}
Ru_c/MgO	700	1.9	8	2.7
	750	1.2	5	2.5
Ru_n/MgO	700	1.6	8.1	3.1
	750	1.6	9.4	3.5
Ru_c/Nb ₂ O ₅	700	2.0	11	3.5
	750	2.4	12	3.6
Ru_n/Nb ₂ O ₅	700	2.5	11.9	3.4
	750	1.9	9.5	3.3

Ru_n/ Nb ₂ O ₅ _500	700	1.8	10	3.4
	750	1.3	7.2	3.4
Ru_c_400/Nb ₂ O ₅	700	2.2	12	3.6
	750	1.8	9	3.4

In general, the WGS activity decreased by increasing the temperature, as $S_{CO_2/CO}$ and H_2/CO values decreased from 700 to 750°C, except for the Ru_n/MgO ($S_{CO_2/CO}$ remained constant, H_2/CO increased) and the Ru_c/Nb₂O₅. ($S_{CO_2/CO}$ and H_2/CO increased). $S_{CO_2/CO}$ values greater than 1 show the presence of the WGS reaction. Greater H_2/CO molar ratios were calculated according to the available data in the literature^{29–31}. A small variation of the $H_2/CH_{4,reacted}$ ratio was observed for all of the catalysts from 700 to 750°C, the Ru_c/MgO showing the lowest values.

The six best catalysts were equally active at 700–750°C. Therefore, the influence of the specific surface area and of the Ru metallic dispersion on catalytic activity was evaluated by BET and CO chemisorption analyses (**Table 5.1**). Among the best performing catalysts no specific relationship can be observed between the catalytic activity, the specific surface area and the metallic dispersion, being the dispersion between 86% for the Ru_n/Nb₂O₅ and < 1% for the Ru_n/Nb₂O₅_500. The metallic dispersion <1% for the Ru_n/Nb₂O₅_500 could indicate that Ru may be present in oxide form on the catalyst surface. The observed order of Ru metallic dispersion is:

Ru_n/Nb₂O₅ > Ru_n/MgO > Ru_c_400/Nb₂O₅ > Ru_c/Nb₂O₅ > Ru_c/MgO > Ru_n/Nb₂O₅_500

The metallic dispersion of Ru remained higher when the Ru nitrosyl nitrate precursor was employed. The low dispersion of the Ru_n/Nb₂O₅_500 could be ascribed to the calcination treatment at 500 °C of the Nb₂O₅ support before the Ru deposition, which caused a huge reduction of the S_{BET} (from 114.7 of the Ru_n/Nb₂O₅ to 43.3 m² g⁻¹ of the Ru_n/Nb₂O₅_500). On the contrary, an

increase of the metallic dispersion was observed for the Ru_c_400/Nb₂O₅ when compared to the Ru_c/Nb₂O₅, as if the calcination treatment after Ru deposition favored the dispersion of Ru on the uncalcined support. MgO-supported catalysts have low S_{BET} of the same order of magnitude. All of the catalysts synthesized presented showed type III isotherm, characteristic of non-porous or macroporous solids, with pore total volumes below 0.05 cm³ g⁻¹.

As no evident relationship between the metallic dispersion and the MSR catalytic activity can be drawn, the catalytic activity could depend upon the structural and surface interaction between the Ru and the support. Thus, XRD (**Figure 5.2**) and SEM (**Figure 5.3**) were used to investigate on the structure and morphology of the best catalysts prepared.

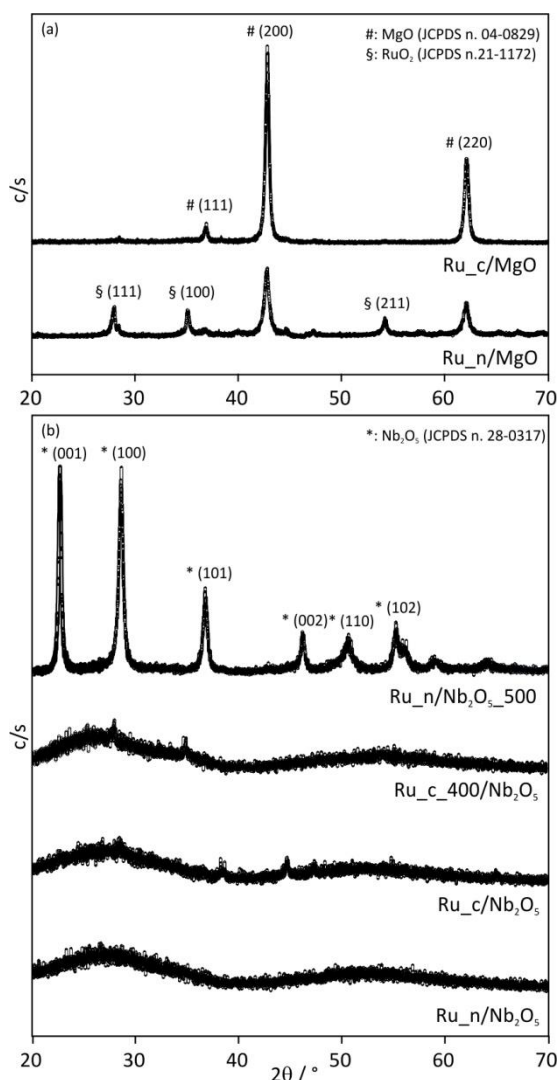


Figure 5.2: XRD patterns of best performing catalysts, (a) Ru/MgO series and (b) Ru/Nb₂O₅ series.

XRD patterns of the Ru_n/MgO and Ru_c/MgO catalysts showed a crystalline structure (**Figure 5.2a**). For the peaks related to the magnesia periclase pure phase (JCPDS card n. 04-0829, $2\theta = 36.88^\circ$, 42.85° , and 62.21°), the MgO-supported catalysts showed peaks to slightly lower degree (Ru_c/MgO at $2\theta = 36.88^\circ$, 42.78° , and 62.05° , while Ru_n/MgO at $2\theta = 36.80^\circ$, 42.80° , and 62.17° , respectively). Rather low intensity peaks for the Ru_n/MgO were observed compared to Ru_c/MgO. Additionally Ru_n/MgO also showed low intensity peaks related to tetragonal RuO₂ at $2\theta = 28.02^\circ$ and 54.3° (JCPDS card n. 21-1172). No such peaks of Ru are visible on Ru_c/MgO. The XRD patterns of the Ru_c/Nb₂O₅, Ru_n/Nb₂O₅ and the Ru_c_400/Nb₂O₅ catalysts (**Figure 5.2b**) show an amorphous structure related to the starting HY-340 precursor^{27,38}. Despite the

calcination treatment at 400°C, the Ru_c_400/Nb₂O₅ still shows an amorphous structure, sign that temperatures below 400°C do not change the structure of niobic acid²³. On the other hand, calcining the support at 500 °C before the Ru depositing caused the formation of the crystalline tetragonal phase of Nb₂O₅ (JCPDS card n. 28-0317)²⁷. The Ru_n/Nb₂O₅_500, in fact, showed peaks at 2θ= 22.60°, 28.56°, 36.73°, 46.23°, 50.65° and 55.24°. The absence of Ru related peaks on the Ru_n/Nb₂O₅_500 could be due to fine dispersion of RuO₂ over the support²⁷.

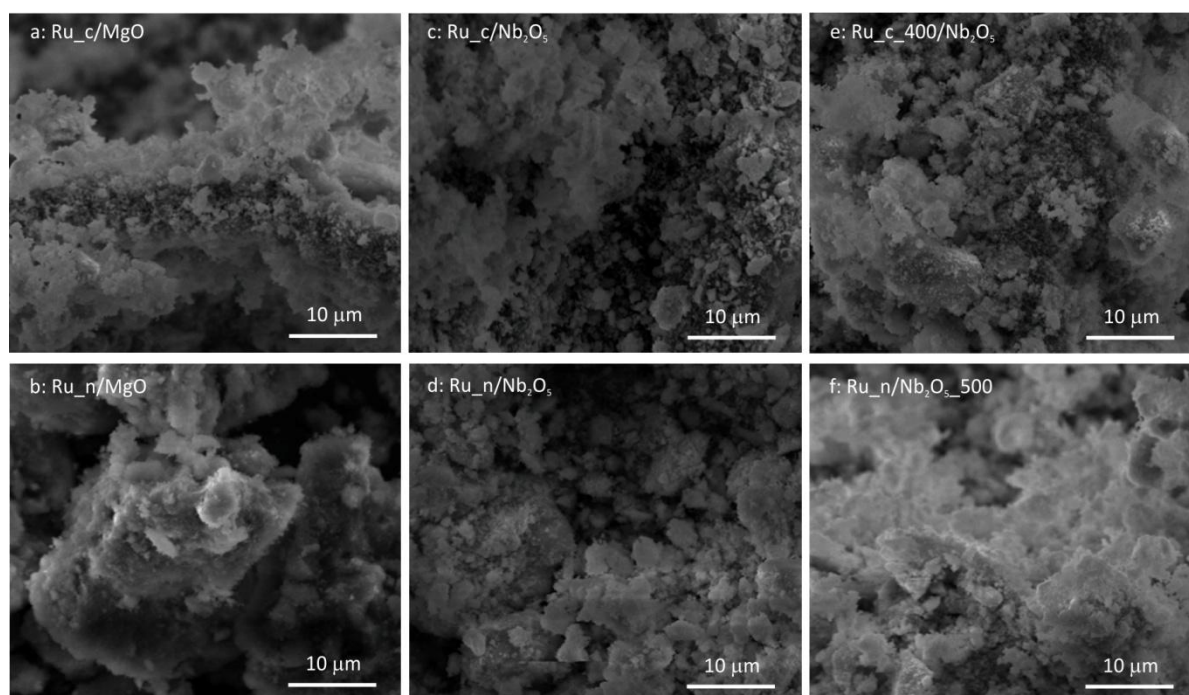


Figure 5.3: SEM micrographs of the best performing catalysts, magnification 6000X.

SEM micrographs showed very similar morphology, not porous, for all of the catalysts observed (**Figure 5.3**), without critical differences. From the structural point of view, XRD and SEM analyses enlightened mixed structure. Three out of the six best performing catalysts were amorphous, while the three heat treated catalysts were crystalline. The catalytic activity in terms of CH₄ conversion appears unaffected by the crystalline/amorphous structure of the catalysts. On the contrary, apparently the structure plays a key role on the H₂ dry outlet concentration and CO₂ selectivity. The Ru_c/Nb₂O₅, Ru_n/Nb₂O₅ and the Ru_c_400/Nb₂O₅ catalysts, in fact, showed an amorphous structure and were

highly selective for CO₂(values between 64 and 71% in the range 700-750 °C), with high H₂ dry outlet concentration (values between 77 and 78% in the range 700-750 °C), while the crystalline structure catalysts Ru_n/MgO, Ru_c/MgO and Ru_n/Nb₂O₅_500 showed lower values (in the range 700-750 °C: S_{CO2} values between 55 and 65%, and H₂ dry outlet concentration values between 71 and 78%, respectively).

Table 5.3: XPS analyses of the best performing catalyst.

Catalyst	Atomic %		Atomic Ratio Ru/Mg or Ru/Nb	Binding energies [eV]				
	Ru	Nb or Mg		Mg 2p	Nb 3d _{5/2}	Nb 3d _{3/2}	Ru 3d _{5/2}	Ru 3d _{3/2}
Ru _c /MgO	2.5	0.1	25.0	49.0	-	-	281.6	284.9
Ru _n /MgO	3.2	0.1	32.0	49.2	-	-	281.9	284.8
Ru _c /Nb ₂ O ₅	1.9	9.1	0.2	-	207.3	210.0	282.4	284.8
Ru _n /Nb ₂ O ₅	3.5	7.1	0.5	-	208.4	211.2	284.8	288.8
Ru _c _400/Nb ₂ O ₅	1.5	11.6	0.1	-	207.2	209.9	279.3	283.6
Ru _n /Nb ₂ O ₅ _500	5.1	2.0	2.6	-	207.4	210.2	284.8	287.2

XPS analysis was then employed to further understand the metal/support interaction over the catalyst surface(**Figure 5.4** and **Table 5.3**) along with the results obtained from EDX (**Table 5.1**).The surface atomic percentage from the general surveys and the calculated surface atomic ratios (Ru/Mg or Ru/Nb)depends upon the preparation conditions of the catalysts. Moreover, for the same preparation conditions and supports, also the choice of the precursor (Ru nitrosyl nitrate or Ru chloride) influences the surface atomic percentage of Ru catalysts. For example, the Ru_n/MgO shows 3.2 at.% Ru compared to the

2.5 at.% for Ru_c/MgO, whereas for the Ru_n/Nb₂O₅ or Ru_c/Nb₂O₅ these values are 3.5 and 1.9 at.%, respectively. Overall, catalysts prepared from Ru nitrosyl nitrate shows higher Ru at.% values (**Table 5.3**). EDX values measured during SEM analyses were on average slightly lower (**Table 5.1**) compared to the XPS values, sign that these catalysts show Ru surface enrichment. When the Nb₂O₅-supported catalyst was calcined at 500 °C before Ru deposition, the Ru at.% was higher (5.1 at.% for Ru_n/Nb₂O₅_500), whereas when the catalyst was calcined at 400 °C after Ru deposition the Ru at.% was lower (1.9 at.% for Ru_c_400/Nb₂O₅). Interestingly, catalysts with amorphous structure (XRD analysis of Ru_c/Nb₂O₅, Ru_n/Nb₂O₅, and Ru_c_400/Nb₂O₅, **Figure 5.2**) exhibited Ru/support atomic ratios < 1, while for the crystalline structure catalysts the Ru/support ratio exceeded 1 structure (XRD analysis of Ru_c/MgO, Ru_n/MgO, and Ru_n/Nb₂O₅_500, **Figure 5.2**).

Figure 5.4a show the high resolution spectra of Mg 2p for the two MgO-supported catalysts. They have only one peak related to Mg 2p, with different binding energy values (**Table 5.3**). These binding energy values are lower than that of bulk Mg 2p value of 49.6 eV³⁹. With a negative shift of the peaks the Mg is present as Mg²⁺^{40,41}, mainly due to hygroscopic nature of MgO¹⁵.

Figure 5.4b shows the high resolution spectra of Nb 3d for the Nb₂O₅-supported catalysts, with the two characteristic 3d_{5/2} and 3d_{3/2} peaks. The values of Nb 3d_{5/2} binding energies are associated with bulk Nb at 207.5 eV^{42,43}. The Ru_n/Nb₂O₅ shows the highest 3d_{5/2} binding energy value (208.4 eV), higher than the pure bulk Nb, sign that this catalyst has more ionic character because of the presence of Nb⁵⁺ on the surface⁴⁴. All the other Nb₂O₅-supported catalysts have lower binding energies compared to the bulk Nb. The analysis of the binding energies of the Nb 3d_{3/2} peak shows columbic interaction and higher oxidation state of Nb³⁶.

Figure 5.4c shows the surface state of Ru for all of the catalysts. The high resolution spectra of Ru consists of two distinct peaks Ru 3d_{5/2} and Ru 3d_{3/2} peaks resulting from spin-orbital splitting⁴⁵. The Ru 3d_{3/2} peak overlaps with C 1s peak (≈284.5 eV): the appearance of C 1s peak is presumably caused by CH_x carbon

impurities present on the sample surface or in the apparatus. Thus, the analysis focused on Ru 3d_{5/2}. For Ru/MgO supported catalysts, which underwent to thermal treatment, Ru⁰, Ru⁺² and Ru⁺⁴ oxidation states are visible. However, for all of the Ru/Nb₂O₅ catalysts the Ru is present mostly in Ru⁺⁴ oxidation state with a shift from bulk Ru⁴⁶. The shift of the Ru 3d peak is often interpreted as a result of electron transfer from the support to supported Ru metal particles⁴⁷.

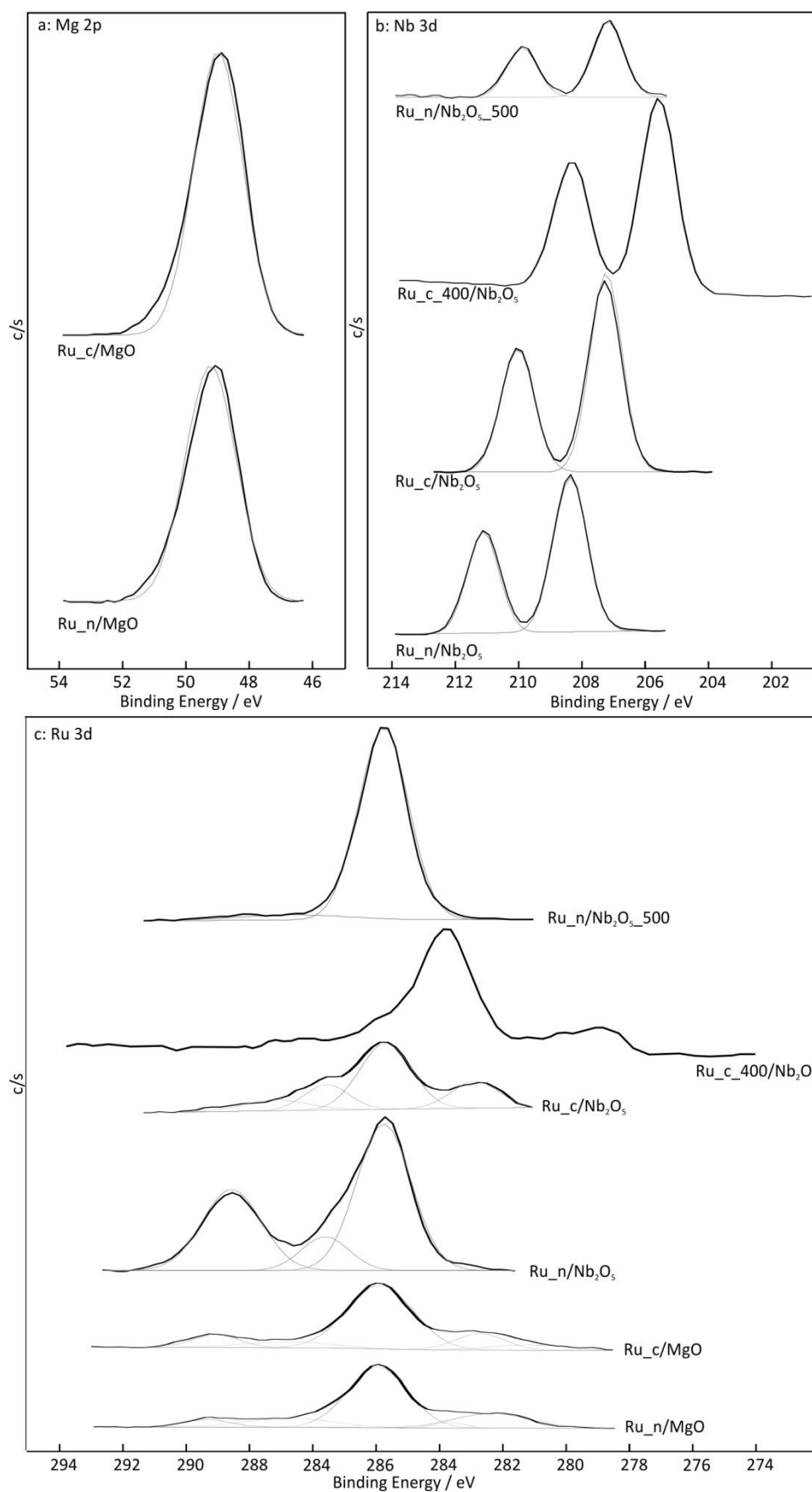


Figure 5.4: XPS high resolution spectra of the best performing catalysts: (a) Mg 2p for Ru/MgO series; (b) Nb 3d for Ru/Nb₂O₅ series; (c) Ru 3d for Ru/MgO and Ru/Nb₂O₅ series.

All the six catalysts showed comparable results. Among them, anyway, the most performing ones are the niobic acid-supported catalyst, with amorphous structure, which provided slightly higher activity at 700 °C, in terms of CH₄ conversion, CO₂ selectivity, and H₂ dry outlet concentration.

5.4 References

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Chapter 6 : A Comparative Study on Steam and Oxidative Steam Reforming of Methane with Noble Metal Catalysts

6.1 INTRODUCTION

Hydrogen generation is one of the most challenging tasks in tomorrow's world of hydrogen economy. With the improvements in fuel cell (FC) technology the call for clean and efficient fuels is becoming far more important. In such a context, auxiliary power units (APUs) are the most promising application for FC technology supplied with hydrogen from fossil fuel reforming.^{1,2} Natural gas is most prominently applied for residential applications, logistic fuels as LPG gasoline and diesel are the premium choice for mobile applications.^{2,3} Recent modeling calculations have shown that the efficiency of APUs decreases in the order of methane > gasoline > light diesel > heavy diesel.⁴ Natural gas is found to be most efficient source to produce hydrogen onboard maintaining maximum fuel cell efficiency,⁴⁻⁶ especially when steam reforming is used.⁷ However, reforming of higher hydrocarbons like diesel, gasoline and LPG, is of particular interest for the production of hydrogen as these fuels are readily available onboard vehicles in automotive systems.⁷⁻⁹ For PEM-FCs in the automotive sector, in fact, one of the major needs is to develop processes for onboard hydrogen production with reduced CO content, in order to reduce the CO clean-up process prior feeding PEM-FCs.^{8,9}

Currently, for hydrogen generation from hydrocarbons, three major approaches prevail: auto thermal reforming (ATR)¹⁰⁻¹⁷ catalytic partial oxidation (CPO),¹⁸⁻²² and steam reforming (SR).^{3,14,16,22-27} SR is a highly energy intensive process and

requires relatively high temperatures to proceed. However, in comparison to the other two processes, it gives the highest yield of hydrogen.²⁸ CPO is highly exothermic and hence does not require any external heat supply. The major drawback of CPO is that hydrogen yield is much lower in comparison to SR. Moreover, because of the high heat generation, hot spot formation can occur resulting in catalyst damage.²⁹ Moreover, CPO and ATR processes are characterized by lower system complexity, whereas SR fuel processors offer the advantage of a larger hydrogen yield and potentially higher system efficiency.⁴ For coupling with a PEM-FC, Cutillo *et al.*¹⁶ concluded that SR appears superior to ATR considering the fuel processor efficiency and hydrogen concentration at the fuel cell inlet.

At present, one of the most important processes at industrial scale to produce hydrogen rich gas from natural gas to feed PEM-FCs is the catalytic SR.¹⁶ Anyway, the oxidative steam reforming (OSR),^{26–34} offers an advantageous alternative route for hydrogen generation, as the addition of a slight amount of oxygen to the SR process provides the advantage of favoring the complete conversion of methane fed to the reactor,^{16,35} by limiting thus the overall energy required by the system, and offers a better response to dynamic changes.^{4,7,16,36–387} OSR is essentially a combination of SR and CPO. The carbon monoxide yield results lower in comparison to SR because of the CO oxidation reaction, whereas the hydrogen yield is in between SR and CPO processes.^{28,30} The OSR process can be made autothermal by properly adjusting the oxygen-to-carbon (O/C) molar ratio. As the O/C molar ratio increases the hydrogen yield decreases, therefore an optimum value of O/C molar ratio must be used to maximize the hydrogen yield and to minimize the CO yield.²⁸ Operating with O/C molar ratios less than 0.7 is generally called OSR.²⁶

Ni catalysts have been industrially used for production of hydrogen through SR with metal concentration as high as 10% on different oxide supports.^{29,39–43} However, Ni-based catalysts are also very active for decomposition of methane to carbon and hydrogen.^{44,45} At high reaction temperature, large amounts of fibrous carbon can be formed, known as carbon whiskers, which influence activity and

stability of the catalyst itself, and can even damage the reactor.³⁹ Due to these constraints, and possible environmental concerns about Ni, researchers are working on alternative catalysts, capable to deliver the same or better catalytic performance compared to Ni, and being possibly cheaper to produce. On these regards, noble metals such as Pt, Pd, Rh, Ru are very active towards SR and OSR reactions and delivers better performance than Ni at very low concentrations.⁴⁶

Extensive studies regarding methane SR and OSR reactions using noble metal catalysts are available in the literature: Pt,^{30,47–49} Ru,^{33,50,51} and Rh,^{26–28,52,53} based catalysts give promising results at low metallic dispersions. Commercial $\gamma\text{Al}_2\text{O}_3$ is used as carrier for noble metal catalysts due to its high specific surface area. But different oxides, pure and in mixed solid solution, are being explored as potential candidates for metal carrier.^{11,40,46–55} CeO_2 , for example, is considered a good carrier due to its oxygen storage capacity and strong interaction with metals thanks to its ability in creating metal-carrier redox couples.^{56–59} The CeO_2 reducibility ($\text{Ce}^{4+}/\text{Ce}^{3+}$) determines a higher specific rate of the supported noble metals, compared to the analogous alumina supported catalysts, particularly in reactions such as water gas shift, steam reforming and dry reforming of methane.^{47,48,56–60}

For example, Mortola *et al.*⁴⁸ by carrying out methane SR over $\text{Pt}/\text{CeO}_2\text{-La}_2\text{O}_3\text{-Al}_2\text{O}_3$ found that a combination of Pt and Ce created $\text{Pt}^0/\text{Pt}^{\delta+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples, which were able to increase methane conversion and coke resistance. Wang *et al.*⁵⁹ by studying methane dry reforming on Rh/CeO_2 catalysts showed that the coexistence of $\text{Rh}^0/\text{Rh}^{\delta+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples facilitated the activation of methane and enhanced the catalytic activity. Methane, in fact, could be activated and dissociated on Rh^0 , releasing electrons to CeO_2 in close contact with Rh^0 and generating the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple. Meanwhile, the electron transfer could also happen from Rh^0 to CeO_2 , creating the $\text{Rh}^0/\text{Rh}^{\delta+}$ couple. Thus, the coexistence of $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Rh}^0/\text{Rh}^{\delta+}$ redox couples promoted CH_4 adsorption and C–H bond cleavage.

In this work Pt, Ru and Rh based catalysts on CeO₂ and Al₂O₃ carriers were prepared, characterized and tested comparatively for methane SR and OSR reactions, respectively.

6.2 EXPERIMENTAL

6.2.1 Catalysts preparations

Two different methods based on solution combustion synthesis (SCS)^{61,62} were used to prepare the studied catalysts.

The Rh and Ru based catalysts were synthesized in two different steps, by employing first the SCS for preparing the carriers (CeO₂ and Al₂O₃), and then the incipient wetness impregnation for depositing the noble metals.^{63,64} For preparing CeO₂ and Al₂O₃ carriers, metal nitrate precursors of desired oxides (cerium nitrate Ce(NO₃)₃·6H₂O, or aluminum nitrate Al(NO₃)₃·9H₂O) and urea (CH₄N₂O) as fuel were placed together in aqueous solution and heated up to 600 °C in a furnace. In these conditions the reaction evolved up to the formation of desired oxides. The so-synthesized powders were then calcined in static air for 3 h at 650 °C. Active metals were deposited on the carriers by incipient wetness impregnation: an aqueous solution of the metal precursor nitrate was prepared and deposited drop by drop on the carrier, meanwhile thoroughly mixing the whole mass at about 130 °C in order to let the water evaporate together with N₂. A final calcination followed in static air for 3 h at 800 °C. The noble metal content of Ru and Rh based catalysts was 1.5% in weight.

Supported 1.1 wt.% Pt/CeO₂ and Pt/Al₂O₃ catalysts were prepared by one-shot oxalyldihydrazide–nitrate self-combustion synthesis, as detailed described in the previous work of Pino *et. al.*³⁰ Briefly, the combustion mixture (containing ceric ammonium nitrate (NH₄)₂Ce(NO₃)₆, or aluminum nitrate Al(NO₃)₃·9H₂O, chloroplatinic acid H₂PtCl₆, and oxalyldihydrazide C₂H₆N₄O₂ as fuel) was dissolved in a minimum volume of water. The dish containing the redox mixture was then introduced into a muffle furnace preheated at 350 °C. The solution boiled with frothing and foaming with concomitant dehydration. At the point of its complete

dehydration, the fuel ignited the redox mixture with a flame temperature of ca. 1000 °C, yielding a voluminous finely dispersed solid product within about 5 min. Prepared catalysts were then calcined in static air for 3 h at 800 °C.

6.2.2 Catalytic Activity

The catalytic activity of the catalyst was evaluated in temperature range of 400-750°C. Details of catalytic activity measurements are presented in **Chapter 2**

6.2.3 Catalysts Characterization:

The catalyst prepared were characterized by BET, CO Chemisorption, XRD, and TEM

6.3 RESULTS

6.3.1 Screening of the catalytic activity performance towards the methane SR reaction

All prepared catalysts were firstly tested towards the methane SR reaction. The obtained results are depicted in **Figure 6.1**.

Concerning Rh-based catalysts (**Figure 6.1 A and B**), the 1.5% Rh/CeO₂ showed the most promising performance, as it reached 96.9% conversion rate with 74.1% at only 585 °C, and full methane conversion with 74.4% outlet hydrogen concentration already at 635 °C, whereas the 1.5% Rh/Al₂O₃ reached full methane conversion with 76.2% hydrogen outlet concentration at a slightly higher temperature, 660 °C. Even by analyzing the carbon dioxide selectivity (**Figure 6.1B**), the 1.5% Rh/CeO₂ showed a slightly better performance compared to the 1.5% Rh/Al₂O₃, reaching a maximum of 87.5% at 635 °C, corresponding to a CO volume concentration of 2.8% in the dry reformat gas, whereas the 1.5% Rh/Al₂O₃ reached a value of 81.8% as carbon dioxide selectivity value at 630 °C (corresponding to a CO volume concentration of 3.9%), and a value of 80.8% as carbon dioxide selectivity at 660 °C

(corresponding to a CO volume concentration of 4.0%), with almost full methane conversion.

By observing the activities of Ru-based catalysts (**Figure 6.1 C and D**), their performance was very similar. The 1.5% Ru/Al₂O₃ performed slightly better than 1.5% Ru/CeO₂ in terms of methane conversion, outlet hydrogen concentration and carbon dioxide selectivity. It reached complete methane conversion at 699 °C (76.8% hydrogen outlet concentration and carbon dioxide selectivity equal to 77.9% with a CO volume concentration of 5.3% in the dry reformat). The 1.5% Ru/CeO₂, instead, did not reach complete conversion at 699 °C, but only 96.8% methane conversion, with 74.8% hydrogen outlet concentration and carbon dioxide selectivity of 74.4%, a CO volume concentration of 5.9% in the dry reformat.

With reference to Pt-based catalysts (**Figure 6.1 E and F**), the 1.1% Pt/CeO₂ performed much better compared to the 1.1% Pt/Al₂O₃, by reaching complete methane conversion with 78.2% hydrogen outlet concentration at 745 °C, with a carbon dioxide selectivity of 61.8%, corresponding to 8.3% CO volume concentration in dry reformat. The 1.1% Pt/Al₂O₃, was not able to reach complete methane conversion at 800 °C.

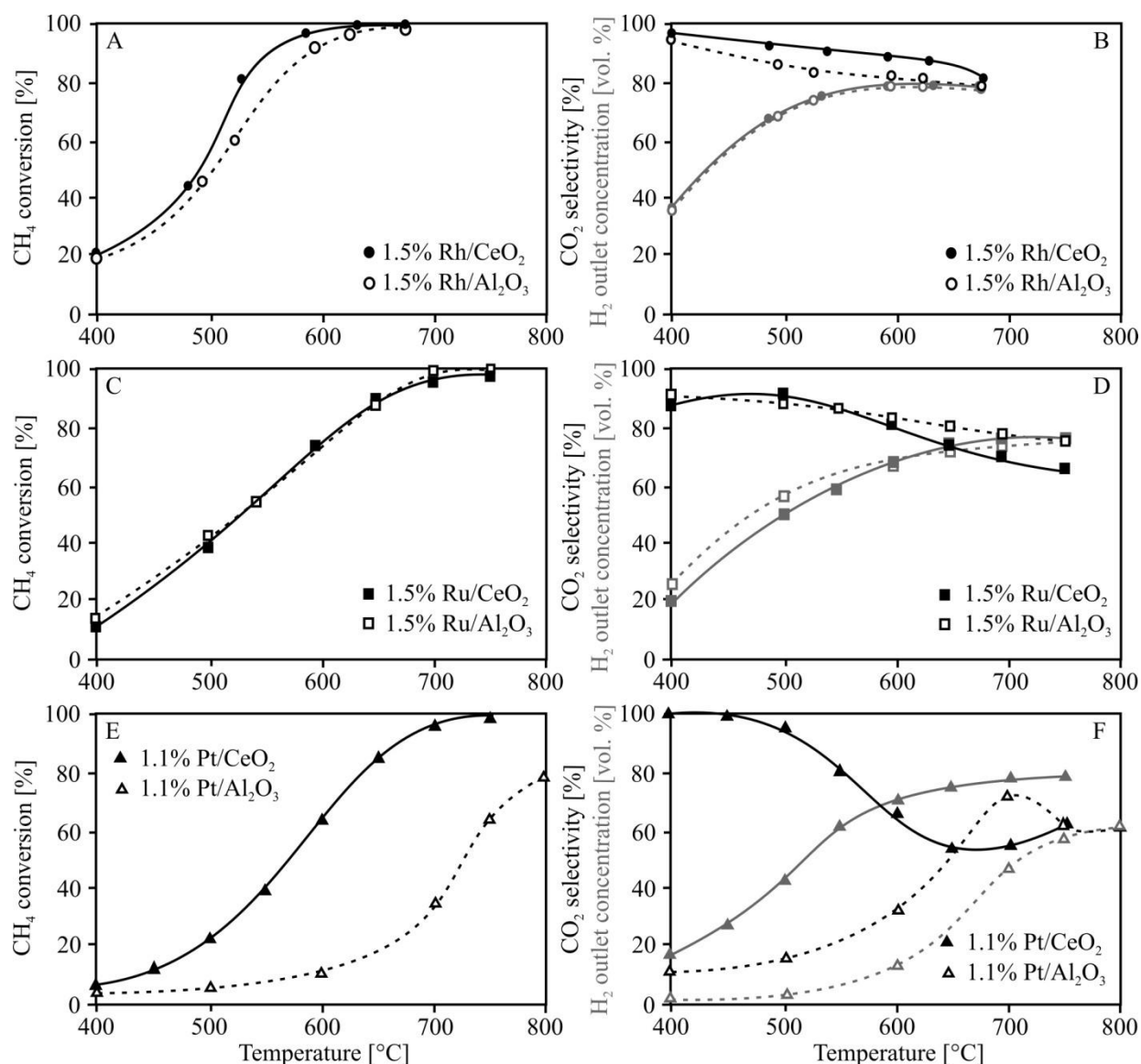


Figure 6.1: Methane conversion (A, C, and E), carbon dioxide selectivity (B, D, and F, black curves) and hydrogen outlet concentration (B, D, and F, gray curves) for all prepared catalysts tested towards methane SR reaction.

By summarizing, among all the tested noble metal catalysts, best performing catalysts towards the methane SR reaction were, respectively, the 1.5% Rh/CeO₂, followed by the 1.5% Ru/Al₂O₃ and the 1.1% Pt/CeO₂. The very promising performance of the 1.5% Rh/CeO₂ can be ascribed to the strong metal support affinity,^{26,56,57} high activity towards water-gas shift reaction,^{63,64} which allowed sensibly reducing the CO fraction in the reformat, and the high noble metal dispersion over the support, as enlighten by the chemisorption and TEM analyses (see **section 6.3.3**). In it worth noting that even if the performance of

the 1.5% Ru/Al₂O₃ and the 1.1% Pt/CeO₂ catalysts were slightly worse compared to 1.5% Rh/CeO₂, their temperature of complete methane conversion was lower compared to those catalysts available in the literature for noble metal based catalysts,^{46,51,65} even if our WHSV was almost half of the one used by Kusakabe *et al.*⁴⁶

6.3.2 Catalytic activity performance of best catalysts towards the methane OSR reaction

Best catalysts from the methane SR reaction screening, i.e, the 1.5% Rh/CeO₂, the 1.5% Ru/Al₂O₃, and the 1.1% Pt/CeO₂, were tested towards the methane OSR reaction. The methane conversion, carbon dioxide selectivity and hydrogen outlet concentration data are reported in **Figure 6.2**.

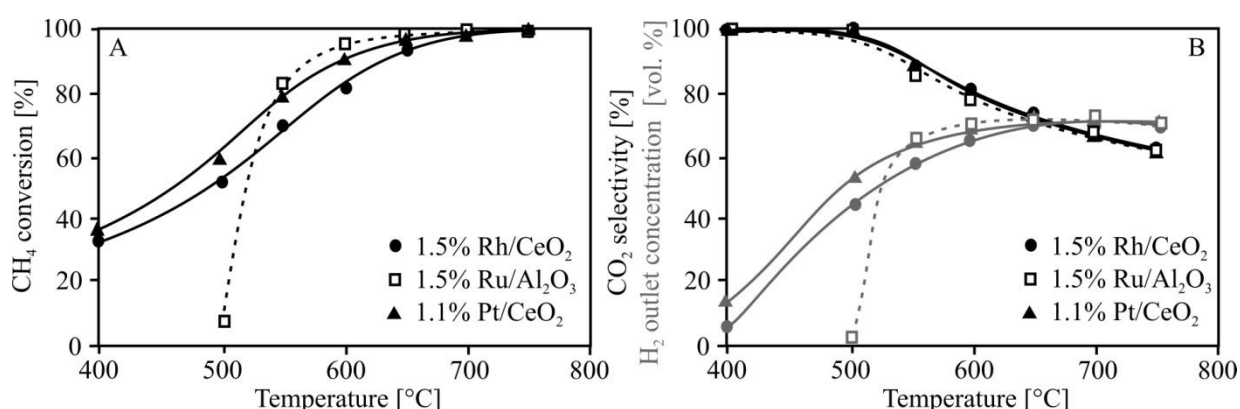


Figure 6.2: Methane conversion (A), carbon dioxide selectivity (B, black curves) and hydrogen outlet concentration (B, gray curves) for the best catalysts tested towards methane OSR reaction.

From **Figure 6.2**, concerning methane conversion data, the catalytic activity of 1.5% Ru/Al₂O₃ was found to be the most promising towards OSR, as it reached complete methane conversion with 68.6% hydrogen outlet concentration at 700 °C, whereas both the 1.5% Rh/CeO₂ and the 1.1% Pt/CeO₂ catalysts reached almost full methane conversion with 68.6% hydrogen outlet concentration at 750 °C. Concerning carbon dioxide selectivity data, displayed in **Figure 6.2B**, all catalysts showed similar values. In particular, the 1.5% Ru/Al₂O₃ catalyst showed the best performance at complete methane conversion: 67.8% carbon dioxide

selectivity at 700 °C with 10.2% residual CO volume concentration in the dry reformat. The 1.5% Rh/CeO₂ and the 1.1% Pt/CeO₂ catalysts showed very similar carbon dioxide selectivity, equal to 63.3% and 62.8%, respectively, with a residual CO volume concentration in the dry reformat of 13.0% and 11.5%, respectively, at 750 °C.

6.3.3 Physical characterization of best catalysts

Best catalysts previously selected from the methane SR and OSR reaction screening, i.e, the 1.5% Rh/CeO₂, the 1.5% Ru/Al₂O₃, and the 1.1% Pt/CeO₂, were fully characterized by means of BET, XRD, CO-chemisorption and TEM analyses.

Table 6.1: Physical characterization of catalysts from BET, CO chemisorption and XRD analyses.

Catalyst	Metal content [wt. %]	S_{BET} [m ² g ⁻¹]	$D_{\%}$ [%]	CeO ₂ crystallite size * [nm]
Rh/CeO ₂	1.5	13.9	22.5	372
Ru/Al ₂ O ₃	1.5	191.5	0.8	-
Pt/CeO ₂	1.1	14.0	12.7	16

* calculated from CeO₂ (1 1 1) using Scherrer Equation

The specific surface area (S_{BET}) and the metal dispersion ($D_{\%}$) measured values for all the catalysts are shown in **Table 6.1**. As expected, the S_{BET} of the Ru-based catalyst was the highest, due to the higher S_{BET} of the Al₂O₃ carrier.⁶⁶ Lower S_{BET} values of Pt- and Rh-based catalysts can be attributed to the CeO₂ carrier.^{67,68}

Regarding the noble metal dispersion, despite the highest S_{BET} displayed by the Ru-based catalyst, the Ru dispersion was the lowest, being less than 1%. Apparently the CeO₂ better favored the dispersion of the noble metal, since the Pt reached a dispersion of 12.7%, and the Rh reached a dispersion of 22.5%.

The highest dispersion value of the Rh could be responsible of the highest catalytic activity recorded during the catalysts screening towards the methane SR reaction.

The analysis of the XRD patterns enlightened interesting results, reported in **Figure 6.3**. For the 1.5% Rh/CeO₂ catalyst (**Figure 6.3A**), only the peaks related to CeO₂ in the fluorite oxide type structure were visible ($2\theta = 28.57^\circ, 33.12^\circ, 47.53^\circ, 56.42^\circ, 59.17^\circ, 69.46^\circ$). A slight shift of these peaks to higher degrees compared to pure CeO₂ (JCPDS card n. 81-0792, $2\theta = 28.54^\circ, 33.07^\circ, 47.47^\circ, 56.33^\circ, 59.07^\circ, 69.40^\circ$) can be envisaged, sign of a change in the lattice parameters, or sign that Rh could be partly incorporated into the CeO₂, forming a solid solution that caused the observable peaks' shift.⁵⁶ Rh peaks (JCPDS card n. 5-0685, $2\theta = 41.06^\circ, 47.78^\circ, 69.87^\circ$) were not visible, a sign that the Rh dispersion is high (see **Table 6.1**).

The XRD diffraction pattern of the 1.5% Ru/Al₂O₃ catalyst (**Figure 6.3B**) showed peaks related to the Ru in its oxidized form (RuO₂ JCPDS card n. 65-2824) and the Al₂O₃ (JCPDS card n. 10-4903) in its amorphous structure. As for the noble metal, only some thin RuO₂ peaks were clearly visible at 2θ equal to $28.22^\circ, 35.24^\circ$, and 54.46° . These peaks resulted slight shifted to higher degree compared to pure RuO₂ ($27.89^\circ, 34.94^\circ$, and 54.03°). Most probably, the calcination temperature in this case affected the interaction between the noble metal and the carrier, which resulted lower compared to other catalysts, causing the oxidation of the Ru.⁶⁹ The presence of Ru in its oxidized form instead of the pure Ru can justify the low metal dispersion recorded by the CO chemisorption analysis (see **Table 6.1**).

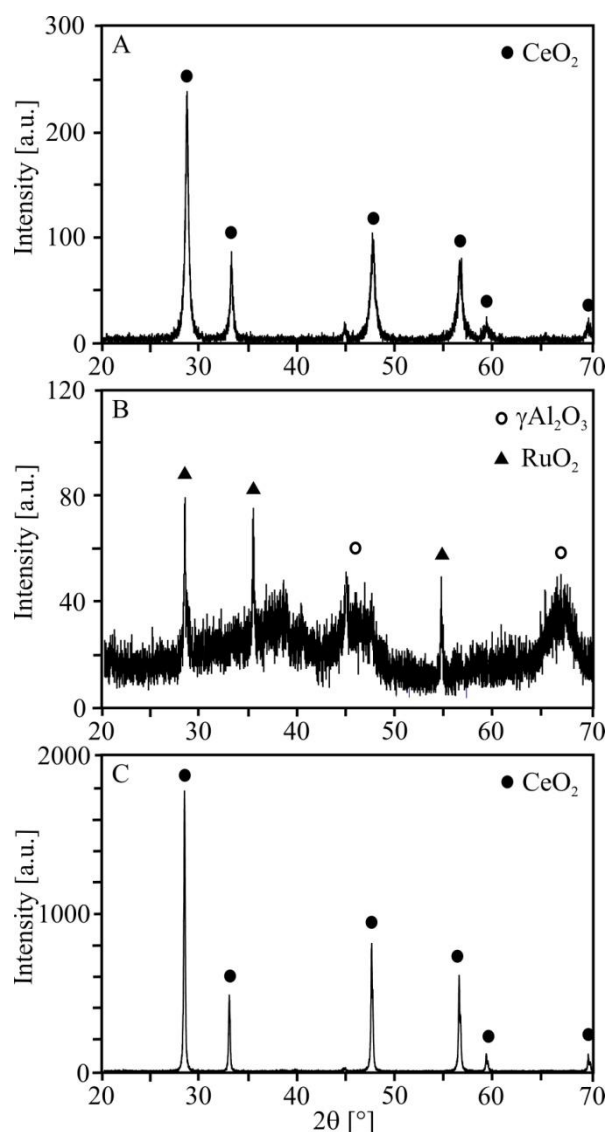


Figure 6.3: XRD patterns for the 1.5% Rh/CeO₂ (A), the 1.5% Ru/Al₂O₃ (B), and the 1.1% Pt/CeO₂ (C) catalysts.

The XRD diffraction pattern of 1.1% Pt/CeO₂ catalyst, shown in **Figure 6.3C**, again the fluorite oxide type structure was identified ($2\theta = 28.59^\circ, 33.14^\circ, 47.58^\circ, 56.47^\circ, 59.24^\circ, 69.54^\circ$), with very high and sharp peaks, sign of a very good degree of crystallinity. Once more, as for the other CeO₂-based catalyst, CeO₂ reflections were slightly shifted to higher degrees with respect to those of pure CeO₂: this observation can suggest the formation of a oxide solid solution.^{30,56} Besides, a scarcely visible broadening peak relative to the crystallographic diffraction of the metallic Pt (JCPDS card n. 4-0802, $2\theta = 39.76^\circ, 46.24^\circ, 67.45^\circ$) can be envisaged only by enlarging the diffraction pattern at 2θ

= 40.01°. This scarcely visible Pt metal phase may be due to the low loading or can denote a relatively high metal dispersion in the obtained catalyst, as enlighten by the data reported in **Table 6.1**.

Figure 6.4 reports some TEM images of the selected best catalysts. The 1.5% Rh/CeO₂ (**Figure 6.4 A and B**) presented well dispersed and small metal particles with size ranging from 5 to 10 nm, and CeO₂ polycrystalline particles ranging from 40 to 400 nm, which is surely consistent with the carrier grain size calculated by the XRD diffraction patterns. The 1.5% Ru/Al₂O₃ (**Figure 6.4 C and D**) evidenced the amorphous phase of the Al₂O₃ carrier, with metal clusters ranging from 5 to even 50 nm. The 1.1% Pt/CeO₂ (**Figure 6.4 E and F**) presented well dispersed and small metal particles with size ranging from 3 to 7 nm, smaller than Rh metal particles on the 1.5% Rh/CeO₂ catalyst, and quite regular CeO₂ polycrystalline particles ranging from 20 to 60 nm. The relatively small Pt particles could be due to the one-shot SCS technique adopted to prepare the Pt-based catalysts, compared to the SCS followed by the wetness impregnation used for the Ru- and Rh-based ones.

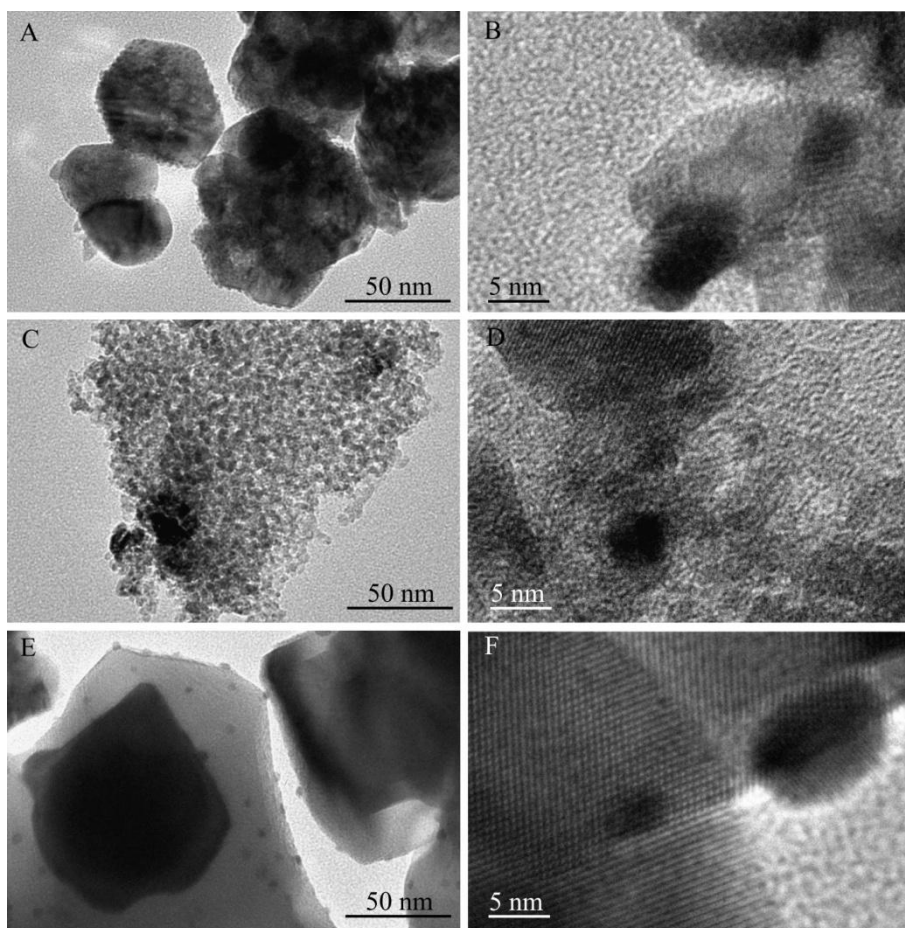


Figure 6.4: TEM images at various magnifications for the 1.5% Rh/CeO₂ (A and B), the 1.5% Ru/Al₂O₃ (C and D), and the 1.1% Pt/CeO₂ (E and F) catalysts.

6.4 DISCUSSION

6.4.1 Comparative analysis of the catalytic activity performance of best catalysts towards the methane SR and OSR reactions

Considering the two best catalysts for the methane SR reaction, that is the 1.5% Rh/CeO₂, and for the methane OSR reaction, that is the 1.5% Ru/Al₂O₃, a deeper comparative analysis on their catalytic performance was carried out in terms of the hydrogen outlet concentration, the ratio of the CO₂ selectivity over the CO selectivity, hydrogen over carbon monoxide molar ratio, and the hydrogen over reacted methane molar ratio.

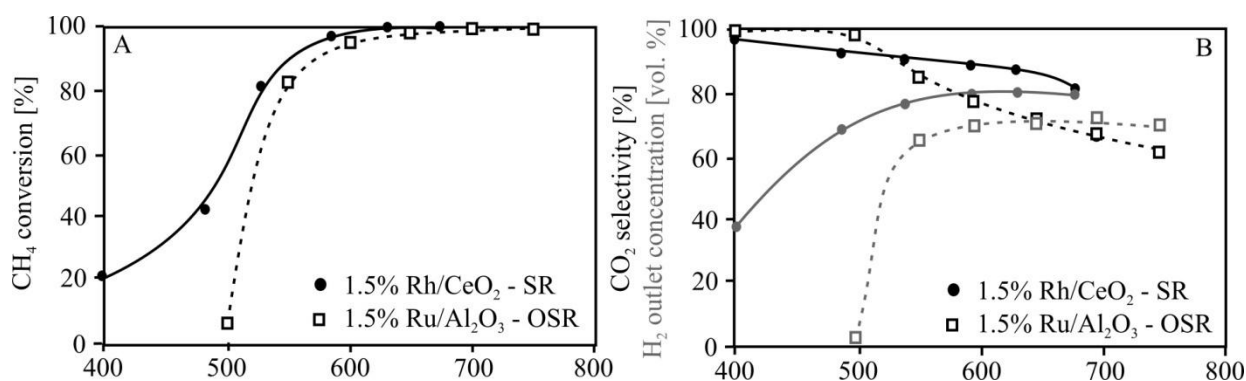


Figure 6.5: Comparative performance in terms of methane conversion (A), carbon dioxide selectivity (B, black curves), and hydrogen volume outlet concentration (B, gray curves) for the best catalysts tested towards methane SR reaction (1.5% Rh/CeO₂) and methane OSR

Figure 6.5 shows the comparative analysis of the two best catalysts in terms of methane conversion, carbon dioxide selectivity, and hydrogen outlet dry volume concentration (already reported in **Figure 6.1** and **Figure 6.2**). It is worth noting that the SR reaction showed better results than the OSR reaction, as the 1.5% Rh/CeO₂ catalysts was able to reach complete methane conversion at lower temperature (635 °C), with a carbon dioxide selectivity of 87.5%, compared to OSR catalyst, which reached complete methane combustion at 699 °C with a carbon dioxide selectivity of 68.6%. Moreover, even the hydrogen generated by the SR reaction was higher as dry volume concentration, being equal to 74.4%, compared to 68.6% reached by the 1.5% Ru/ Al₂O₃ catalyst at 699 °C. The 1.5% Rh/CeO₂ catalyst always displayed a better methane conversion, carbon dioxide selectivity and outlet hydrogen concentration in the whole examined temperature range.

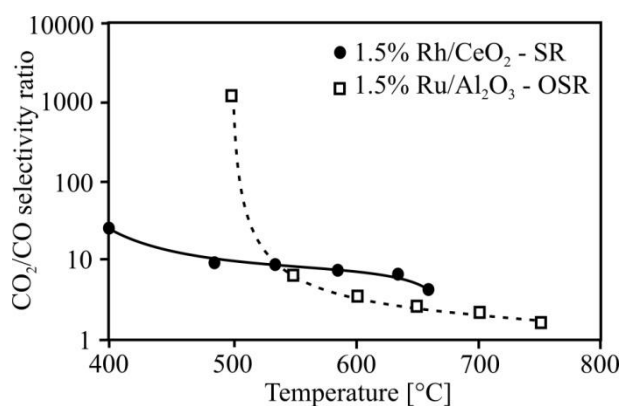


Figure 6.6: Comparative performance in terms of the ratio between the CO₂ selectivity and the CO selectivity for the best catalysts tested towards methane SR reaction (1.5% Rh/CeO₂) and methane OSR reaction (1.5% Ru/ Al₂O₃).

The ratio between the carbon dioxide selectivity and the carbon monoxide selectivity for the two best selected catalysts are compared in **Figure 6.6**. At low temperature both catalysts are highly selective towards carbon dioxide formation, which is the main goal to be pursued within this study. Anyway, the 1.5% Rh/CeO₂ for methane SR reaction remains more selective at high temperature than the 1.5% Ru/ Al₂O₃ catalyst for methane OSR reaction, a sign that probably the water gas shift reaction still occurred in a certain extent. This aspect was noted for steam reforming and dry reforming noble metal catalysts even by other authors.^{58–60} Most probably the reducibility of the CeO₂ carrier plays a crucial role in interacting with the noble metal to determine higher specific rates of carbon dioxide formation, compared to the Al₂O₃ carrier.^{57–60}

The H₂/CO molar ratio for the two best catalysts was compared, and reported in **Figure 6.7**. The 1.5% Rh/CeO₂ for methane SR reaction always displayed a higher value of the H₂/CO molar ratio compared to the 1.5% Ru/ Al₂O₃ for methane OSR reaction. For both catalysts this ratio decreased with the temperature increase. In the case of the 1.5% Rh/CeO₂ catalyst, high values of molar ratio can be assigned to the strong metal/support interaction between Rh and CeO₂,^{56,63,64}

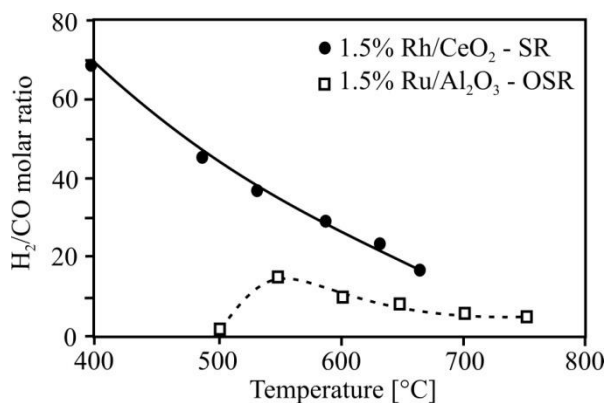


Figure 6.7: Comparative performance in terms of the molar ratio between the H₂ and the CO for the best catalysts tested towards methane SR reaction (1.5% Rh/CeO₂) and methane OSR reaction (1.5% Ru/Al₂O₃).

Considering the hydrogen produced per mol of reacted methane, expressed by the molar ratio between the hydrogen and the reacted methane reported in **Figure 6.8**, the 1.5% Rh/CeO₂ catalyst presented the highest values, which are slightly higher than 3 at high temperature. The theoretical ratio for the SR reaction is equal to 3, thus these slightly higher values of the SR catalyst suggests that the water-gas shift reaction contributes in enhancing the hydrogen produced per mol of reacted methane. For the OSR catalyst, instead, the value of this ratio is almost 2 at high temperature. This suggests that the oxygen present in the feed stream reacts first with the methane to provide carbon dioxide and water (in fact, at low temperature, no hydrogen neither carbon monoxide were present in the reacted gases, see **Figure 6.5**), then probably the dry reforming reaction occurs, letting the un-reacted methane reacting with the formed carbon dioxide thanks to the heat developed by the total oxidation reaction, with the formation of hydrogen and carbon monoxide. The theoretical ratio between the produced hydrogen and the reacted methane for the dry reforming is equal to 2, in fact. Moreover, considering that in the OSR process an increase of the O/C molar ratio causes a decrease of the hydrogen yield,^{26,28} it is not surprising in the present case that the 1.5% Ru/Al₂O₃ catalyst for the OSR reaction, which worked with a relatively high O/C ratio, showed lower H₂/CO and H₂/CH_{4,reacted} molar ratios compared to the 1.5% Rh/CeO₂ catalyst for the SR reaction

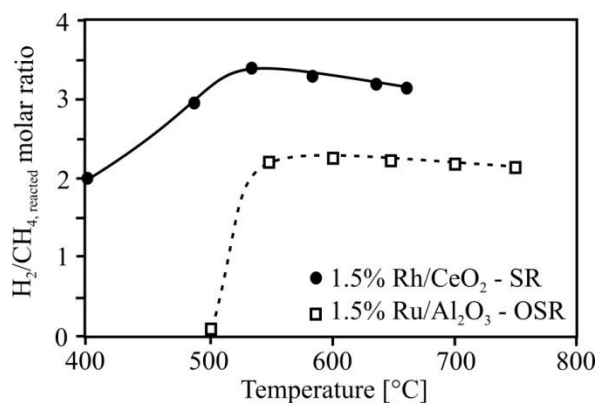


Figure 6.8: Comparative performance in terms of the molar ratio between the H₂ and the reacted CH₄ for the best catalysts tested towards methane SR reaction (1.5% Rh/CeO₂) and methane OSR reaction (1.5% Ru/Al₂O₃).

Both the Rh and Ru are considered in the literature as highly active in SR and OSR among all the noble metals:^{27,28,33,39,48,50,51,59,70–73} their activities are usually on the same scale but depend on the reaction conditions. The addition of oxygen enhances the methane conversion in case of Ru catalyst but decreases in case of Rh. At low temperatures, below 500 °C, the addition of oxygen has a positive effect on Rh, but with the increase in temperature the conversion lowers for OSR than SR. In OSR conditions the Rh catalyst shows high carbon monoxide selectivity and low hydrogen concentrations. Mortola *et al.*⁴⁸ showed that when oxygen concentration is low over the catalyst surface during partial oxidation, the formation of carbon monoxide and hydrogen is favored and low H₂/CO molar ratio shows the occurrence of reverse water gas shift reaction. Cavallaro *et al.*⁷³ found that addition of oxygen promotes metal sintering causing the formation of hotspots, which reduce the Rh metal activity.

In conclusion, the 1.5% Rh/CeO₂ catalyst for methane SR reaction can be selected as the most suitable catalyst for producing a syngas containing the highest hydrogen concentration, and the lower carbon monoxide concentration, as the catalyst was very selective towards the formation of carbon dioxide. This would be very appropriate in case of fuel processors where it is necessary to minimize as much as possible the residual carbon monoxide concentration, for feeding PEM-FCs, as the following CO clean-up process can be reduced. The very

promising performance of the 1.5% Rh/CeO₂ can be ascribed to the strong metal support affinity,⁵⁶ high water-gas shift reaction ability,^{63,64} which allowed sensibly reducing the CO fraction in the reformat, and the high noble metal dispersion over the support, as enlightened by the CO chemisorption and TEM analyses.

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Part II: Catalytic Stability

In the second part of this thesis, after evaluating the catalytic activity and performance of different noble metal catalysts (Ru, Rh and Pt), two best catalysts were chosen and their stability were evaluated. Part II consists **Chapter 7** and **Chapter 8** dealing with the endurance of these catalysts.

Chapter 7 deals with the stability of 1.13% Pt catalyst over CeO₂ support.

Chapter 4 deal with the stability of 1.4% Rh catalyst over CeO₂ support.

Chapter 7 CeO₂ supported Pt catalyst for Methane steam reforming: Catalytic Activity and Stability

7.1 Introduction:

Global warming increase and depleting oil reservoirs call for an alternative environmental friendly energy resource. Hydrogen due to its high energy content and zero emission after combustion can potentially replace the conventional fuels¹⁻³. Hydrogen production on a small scale is the major shortcoming in this scenario. Commercially hydrogen is produced along with CO and CO₂ from methane via steam reforming reaction^{1,4}. According to US department of energy the MSR can provide an initial step towards hydrogen economy.

Steam reforming is an endothermic process and thus requires a high energy input. MSR is preferred among other technologies like partial oxidation, autothermal reforming, oxidative steam reforming and coal gasification⁵ due to its energy efficiency (83%) with lowest hydrogen cost. Steam reforming also provides excellent H₂ concentration with good fuel processor efficiency⁶. Commercially Ni is used as a catalyst for MSR but the issues of sintering and carbon deposition are high on Ni catalyst. Also ageing reduces the porosity and Ni content therefore deactivating the catalyst and results in increase in operating temperature and pressure⁷. Noble metals are potential alternative for Ni in the MSR reaction, as the amount of Ni varies from 10% on commercial catalyst⁸⁻¹² while a small amount of noble metal can produce even better results¹³ and remain active for long time period.

Noble metals like Rh^{14–17}, Pt^{18–27}, Ru^{28–32}, Pd^{33–35} and Ir^{36,37} have been widely studied for methane steam reforming. There is a constant debate regarding order of activity among noble metals³⁸ and Rh and Ru are considered to be most active, but according to study conducted by Wei and Iglesia³⁹ Pt is most active among noble metals for the activation of C-H bond during reforming reaction. De Souza et. al.⁴⁰ studied Pt promotion effect on 10% Ni/Al₂O₃ for MSR finding that Pt addition decreases the reduction temperature by 200°C–300°C and metallic dispersion also decreases by adding the Pt but the catalytic activity increases.

Usually Noble metals are supported on inert supports like Al₂O₃, but CeO₂ supported noble metals are being considered due to oxygen storage capacity, strong metal support interaction, soot resistance and the CeO₂ reducibility (Ce⁴⁺/Ce³⁺). These properties of CeO₂ helps in determining a higher specific rate of the supported noble metals, compared to the usual inert oxide supported catalysts, particularly in reactions such as water gas shift, steam reforming and dry reforming of methane. According to the J. Xu et.al.⁴¹, the CeO_x (x = 2 or 1.5) accelerate the reaction of steam with adsorbed carbon species on the metal surface at the metal–oxide interface, so, the surface carbon species can be quickly converted to gaseous products, preventing accumulation due to the ceria capacity of remove deposited carbon species via gasification by the O species supplemented from the lattice oxygen of the catalyst itself.

Pt/CeO₂ catalyst has been extensively studied for CO oxidation, oxidative methane steam reforming^{26,42}. Mortola et. al.²⁵ carried out MSR over Pt/CeO₂-La₂O₃-Al₂O₃ and found that combination of Pt and Ce create Pt⁰/Pt^{δ+} and Ce⁴⁺/Ce³⁺ redox couples which gives increased methane conversion and carbon resistance over Pt catalyst.

In this work Pt catalysts supported on CeO₂ was synthesized, characterized and its catalytic activity towards MSR reaction was tested. Furthermore, the stability of the catalyst was also evaluated in cyclic conditions. The results of the reforming analysis were also compared with the equilibrium concentrations simulated through sensitivity analysis using AspenPlus^{TM43} software.

7.2 Experimental

7.2.1 Catalysts preparations

Supported 1.13 wt.% Pt/CeO₂ catalyst was prepared by oxalyldihydrazide–nitrate self-combustion synthesis. The combustion mixture contained ceric ammonium nitrate [(NH₄)₂Ce(NO₃)₆], chloroplatinic acid (H₂PtCl₆) and oxalyldihydrazide (C₂H₆N₄O₂) as fuel (molar ratios 0.99:0.01:2.33) was dissolved in a minimum volume of water in a borosilicate dish of 130 cm³ capacity. The dish with this redox mixture was then introduced into a muffle furnace preheated at 350 °C. The solution boiled with frothing and foaming with concomitant dehydration. At the point of its complete dehydration, the fuel ignites the redox mixture with a flame temperature of ca. 1000 °C, yielding a voluminous finely dispersed solid product within about 5 min.

The prepared catalyst was calcined in air at 800°C for 3 h.

7.2.2 Catalytic Activity

The catalytic activity of the catalyst was evaluated in temperature range of 400-750°C. Details of catalytic activity measurements are presented in **Chapter 2**

7.2.3 Catalysts Characterization:

The catalyst prepared were characterized by CO Chemisorption, XRD, SEM EDX and XPS analysis

7.3 Results & Discussion

7.3.1 Fresh Catalyst Characterization

7.3.1.1 BET and CO Chemisorption results

BET and CO chemisorption of the fresh catalyst are presented in **Table 7.1** The Pt/CeO₂ catalyst showed a surface area of 14m²/g compared to other steam reforming catalysts available in literature⁴⁷. This low surface area can be due to the effect of CeO₂ support as it results in low surface area. The metallic

dispersion of 12.7% with 8.9nm crystallite size indicate the fine metal particle dispersion on CeO₂ carrier.

Table 7.1: Physiochemical properties of as prepared 1.13%Pt/CeO₂

Surface Area:	14.0 m ² g ⁻¹
Metal Dispersion: d	12.7 %
Pt Crystallite Size D from metal dispersion=(1/d)	7.89 nm
Metallic Surface Area:	0.31 m ² /g sample
Metallic Surface Area:	31.31 m ² /g metal
Pt Crystallite Size (CO Chemisorption)	8.93 nm

7.3.1.2 XRD results

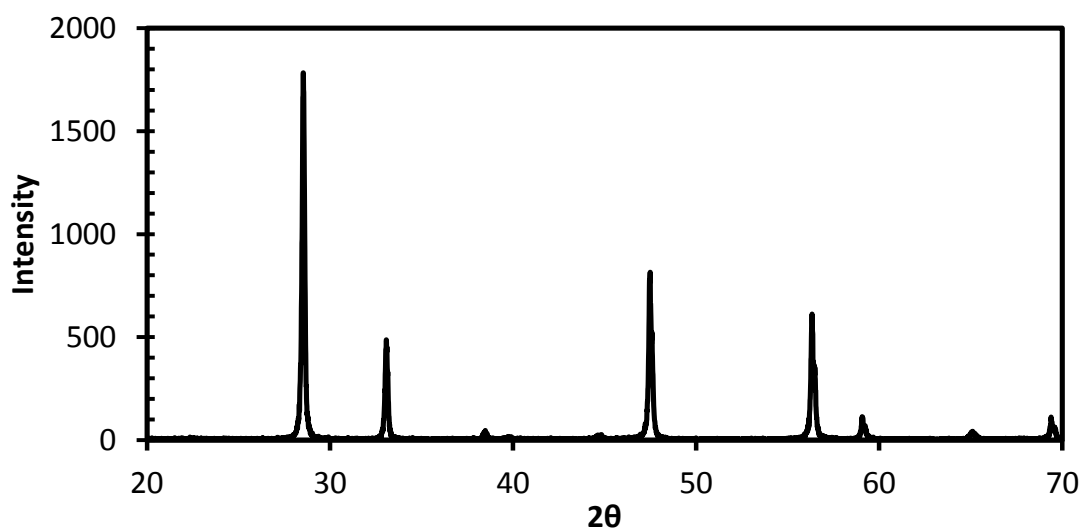


Figure 7.1: XRD pattern of 1.13% Pt/CeO₂ 20-70° as prepared catalyst

X-ray diffractogram of as prepared 1.13% Pt/CeO₂ catalyst (see **Figure 7.1**) indicate a fluorite type CeO₂ structure with the reflections at $2\theta = 28.52^\circ, 33.06^\circ, 47.4^\circ, 56.32^\circ, 59.08^\circ$ and 69.40° . A slight shift of these peaks to a lower degree ($2\theta \sim 0.02^\circ$) compared to pure CeO₂ (JCPDS card n. 81-0792, $2\theta = 28.54^\circ, 33.07^\circ, 47.47^\circ, 56.33^\circ, 59.07^\circ, 69.40^\circ$) is observed. This slight shift to lower degree can be related to two principal factors:

a) the thermal defect generated in the CeO₂ structure during SCS can induces a lattice expansion (shifting the 2θ position to lower angles)^{45,46}

b) a partial substitution of $\text{Pt}^{2+}/\text{Pt}^{4+}$ in the ceria lattice can determine a shrinkage of the lattice (shifting the $2\cdot$ position to high angles).

The combination of this effects can induce, in the current sample a lattice expansion, the related cell parameter of CeO_2 for 1.13 wt %Pt/ CeO_2 is $a=5.415\text{\AA}$ which is slightly higher than the pure CeO_2 ($a=5.411\text{\AA}$)

It is probable that during SCS the Pt ions are added in CeO_2 lattice thus shifting reflections to slightly low degree and increasing lattice parameter. Besides CeO_2 reflections a scarcely visible reflection ($2\theta=39.765^\circ$) is also present related to metallic Pt and is usually present when Pt/ CeO_2 catalyst is synthesized by SCS also shown by other researchers^{26,42,48,49}. The related CeO_2 crystallite size derived from $\text{CeO}_2(200)$ reflection by application of Scherrer equation is 102nm.

FESEM & TEM results

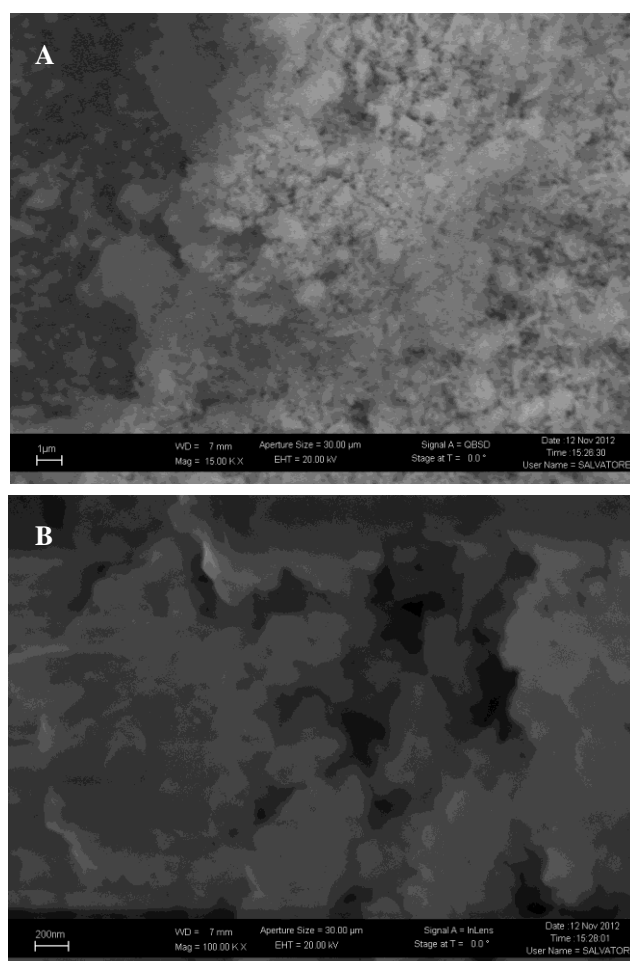


Figure 7.2: FESEM image of as prepared 1.13% Pt/ CeO_2

The surface morphology of fresh catalyst is presented in **Figure 7.2** and **Figure 7.3**. The FESEM micrograph (see **Figure 7.2 A and B**) shows uniform porous structure and integrated texture. Macropores are visible all over the catalyst surface and no metal particles are detectable on a magnification level of 20nm indicating fine dispersion.

TEM images (see **Figure 7.3A and B**) show a low contrast micrograph due to similar masses of CeO₂ and Pt. The CeO₂ crystal size is about 100-150nm good agreement with XRD calculation and Pt crystal size is about 2-7 nm which is in good agreement with CO chemisorption results (see **Table 7.1**). No catalyst agglomerates are visible

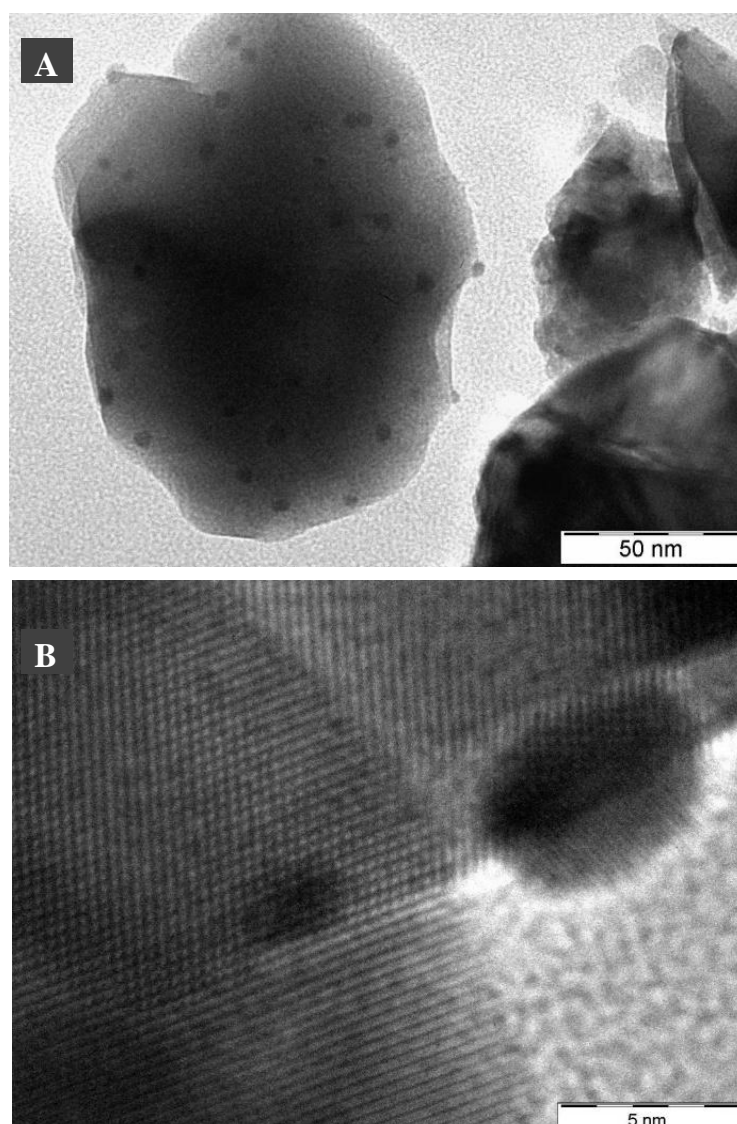


Figure 7.3: TEM image of as prepared catalyst

X-ray Photoelectron Spectroscopy results

To better understand the metal support interaction on the catalyst surface the XPS analysis was carried out and the surface atomic composition is summarized in **Table 7.2**.

Table 7.2: Atomic Percentages from XPS analysis

Samples	Surface Atomic %			Ratio	O _H	O _L	Ce ³⁺	Pt ⁰	Pt ⁺²
	Ce	O	Pt	Pt/Ce	%	%	%	%	%
Fresh (0 h)	10.4	50.3	0.8	0.077	20.13	79.87	23.43	50	50
Used (150 h)	9.5	55.3	0.1	0.011	26.53	73.47	25.55	67	33

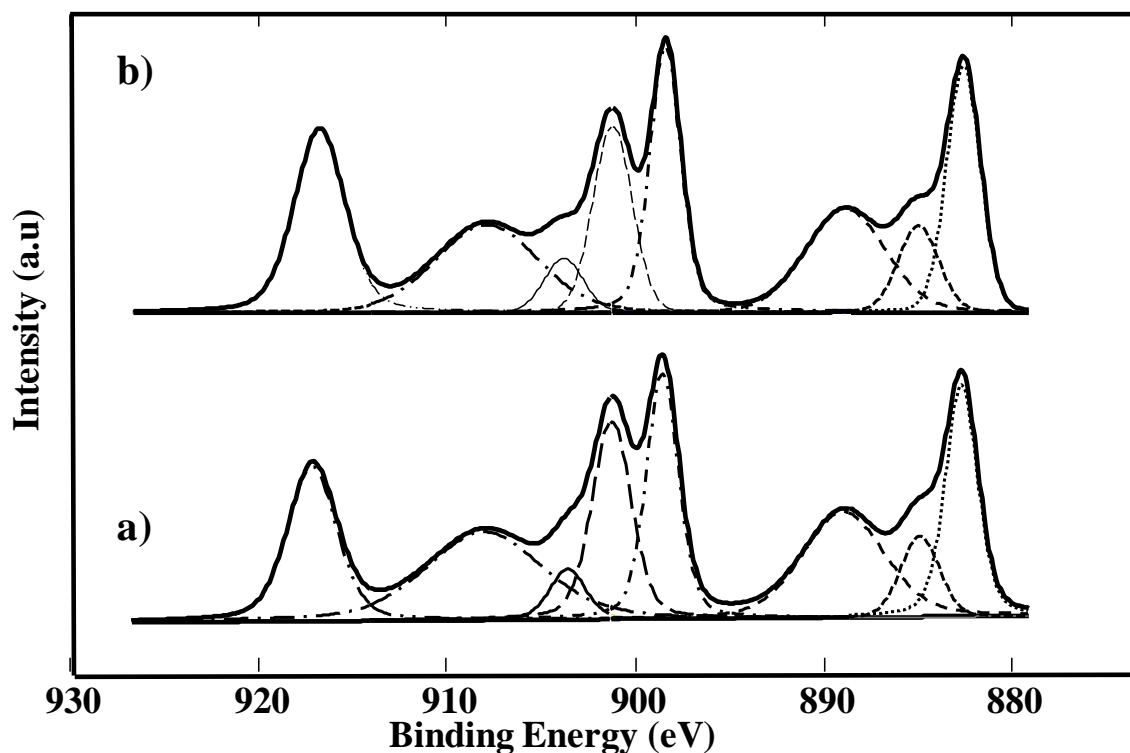


Figure 7.4: XPS Spectra of Ce 3d for Pt/CeO₂ catalyst a) fresh catalyst, b) aged catalyst after 150h

Ce (3d) peaks in B.E range 875-925 eV of as prepared catalyst are given in **Figure 7.4a**. Ce spectra consists of eight peaks which corresponds to four pairs of spin orbitals doublets. Ce (3d_{5/2,3/2}) peaks at 882.6 and 901.2 eV with characteristic satellite marks (see **Figure 7.4a**) corresponds to CeO₂ with Ce in

+4 oxidation state. Surface proportion of Ce^{3+} , estimated according to typical procedure⁵⁰ is presented in **Table 7.2**. It is interesting to note that in the as prepared catalyst contain only 23% Ce^{3+} .

The Pt 4f XPS spectrum of as prepared catalyst is presented in **Figure 7.5a** and the atomic percentage is presented in **Table 7.2**. Pt metal particles ($4f_{7/2,5/2}$) peaks are observed at 71.08 and 74.4 eV respectively. XPS spectra of Pt 4f core level peaks can be resolved into two sets of spin orbitals doublets containing Pt^0 and Pt^{+2} state. The $4f_{7/2}$ binding energy peaks can be deconvoluted into two peaks at 71.08 eV and 72.87 eV while $4f_{5/2}$ binding energy peaks are visible at at 74.44 eV and 76.12 eV. The peaks at 71.08 eV and 74.44 eV can be assigned to Pt^0 state⁴², while peaks at 72.87 eV and 76.12 eV can be assigned to the presence of PtO. However, in as prepared catalyst the ratio of Pt^0 : Pt^{+2} is 50:50 (see **Table 7.2**).

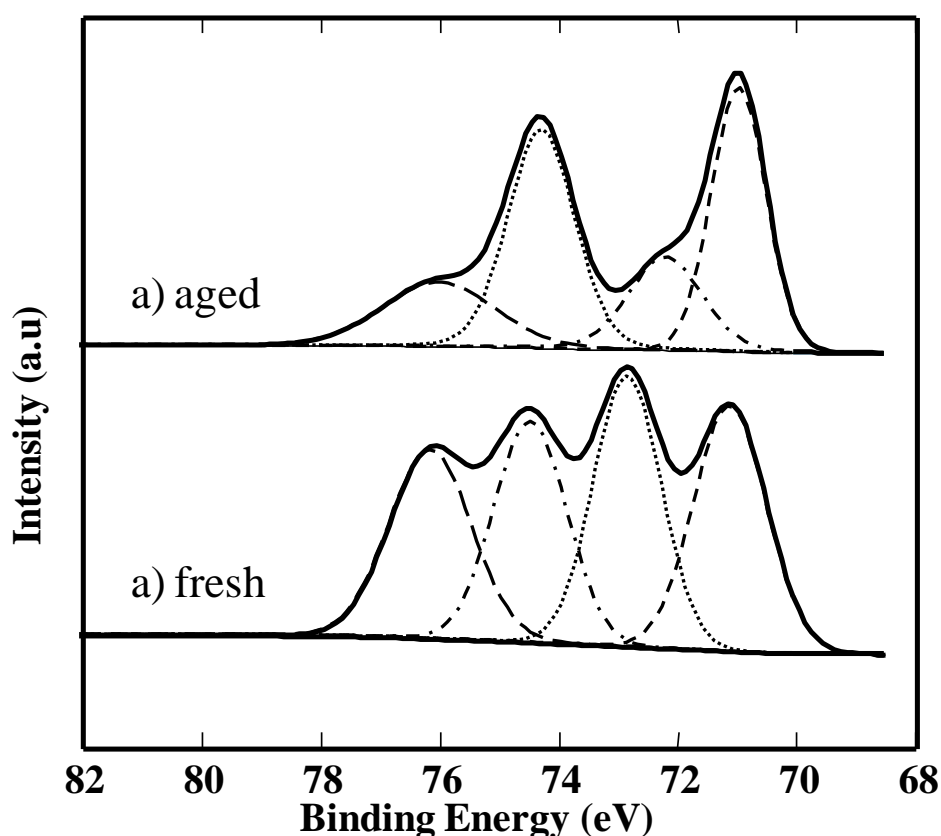


Figure 7.5: XPS Spectra of Pt4f for Pt/CeO₂ catalyst a) fresh catalyst, b) aged catalyst after 150h

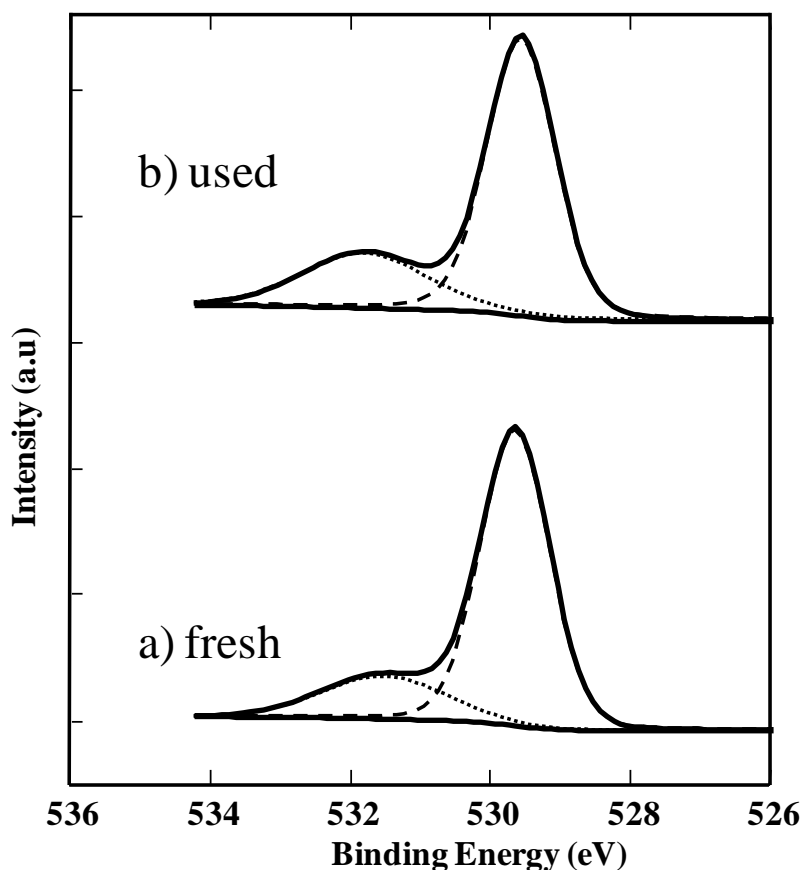


Figure 7.6: XPS Spectra of O1s for Pt/CeO₂ catalyst a) fresh catalyst, b) aged catalyst after 150h

O1s XPS profile of as prepared catalyst is shown in **Figure 7.6a** and exhibits two binding energies at 529.6 eV and 532 eV respectively. The binding energy of 529.6 eV can be assigned to the surface lattice oxygen (O_L) of ceria, while 532eV represents chemisorbed surface oxygen (O_H). The surface oxygen percent of surface and chemisorbed oxygen is presented in **Table 7.2**. Higher O_H concentration verifies the rich presence of chemisorbed surface oxygen species that generally act as the most reactive oxygen species⁵⁰

7.3.2 Catalyst Activity:

7.3.2.1 Effect of WSV:

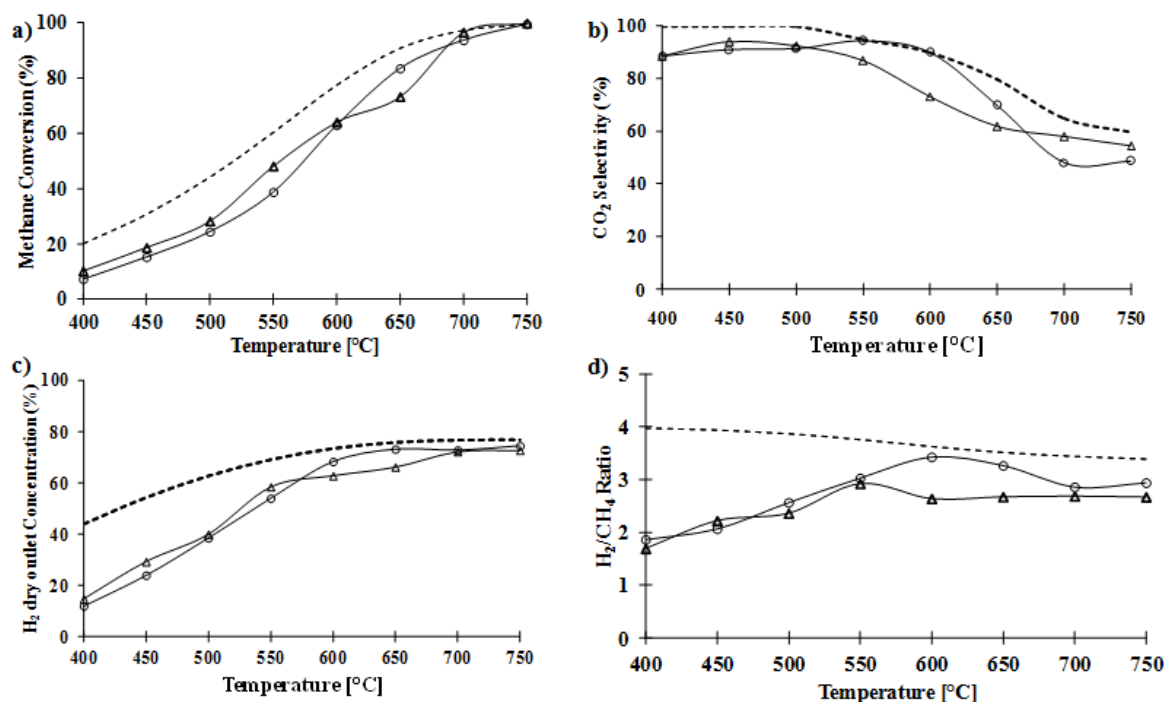


Figure 7.7: Temperature Effect on catalytic activity at different WSV and constant S/C ratio 3, a) methane conversion, b) CO₂ selectivity, c) H₂ dry outlet concentration, d) H₂/CH₄. Δ = 27.65, \circ = 20, -- = equilibrium values

Firstly the effect of WSV on catalytic activity of Pt/CeO₂ at S/C 3 in temperature range of 400 -750°C was evaluated as presented in **Figure 7.7(a-d)**. The WSV was changed from 0.33NL-min⁻¹-g_{cat}⁻¹ (hereafter called "low WSV") to 0.46NL-min⁻¹-g_{cat}⁻¹ (hereafter called "high WSV") by changing the flow rate of gas mixture while the weight of the catalyst was kept constant.

In general the increase in WSV showed a slight decrease in catalytic activity in terms of methane conversion and H₂ dry outlet concentration (see **Figure 7.7 a and c**). Below 500°C the methane conversion and H₂ dry outlet concentration was slightly higher at high WSV but at 500 and 550°C the values were similar for both high WSV and low WSV. After 550°C the methane conversion remained slightly higher at low WSV as the catalyst achieved 97% and 100% methane conversion at 700 and 750°C respectively.

The temperature increment showed a negative effect on the CO₂ selectivity and low WSV favored the CO₂ selectivity (see **Figure 7.7 b**). At low WSV Increase in

the temperature from 400°C to 650°C resulted in a gradual decrease of CO₂ selectivity from 100% to 56% respectively, however after 650°C the catalyst showed improvement as it achieved 65% CO₂ selectivity at 750°C. High WSV, however disfavored the CO₂ selectivity of the catalyst achieving 88% CO₂ selectivity at 400°C and decreased down to 49% at 750°C. Variation of WSV resulted in higher CO₂ selectivity as compared to equilibrium calculations. Increase in CO₂ selectivity even at higher temperature can be attributed to water gas shift reaction^{50,51} along with CO oxidation characteristics of Pt/CeO₂^{47,52}.

By increasing WSV the contact time of reaction mixture and the catalyst is decreased thus effecting the methane conversion and H₂ dry outlet concentration. At low WSV the contact time is high therefore the catalyst achieved higher methane conversion, H₂ dry outlet concentration and H₂/CH_{4,reacted} molar ratio. At high WSV the influence of WGS reaction is minimized due to slow reaction rate⁵³ therefore resulting in low CO₂ selectivity and low hydrogen content. That's why the H₂/CH_{4,reacted} molar ratio remained low at high WSV (see **Figure 7.7d**)

In comparison to equilibrium values the catalyst showed values lower than equilibrium till 650°C after which the catalyst achieved reaction equilibrium (see **Figure 7.7**)

7.3.2.2 Effect of S/C Ratio:

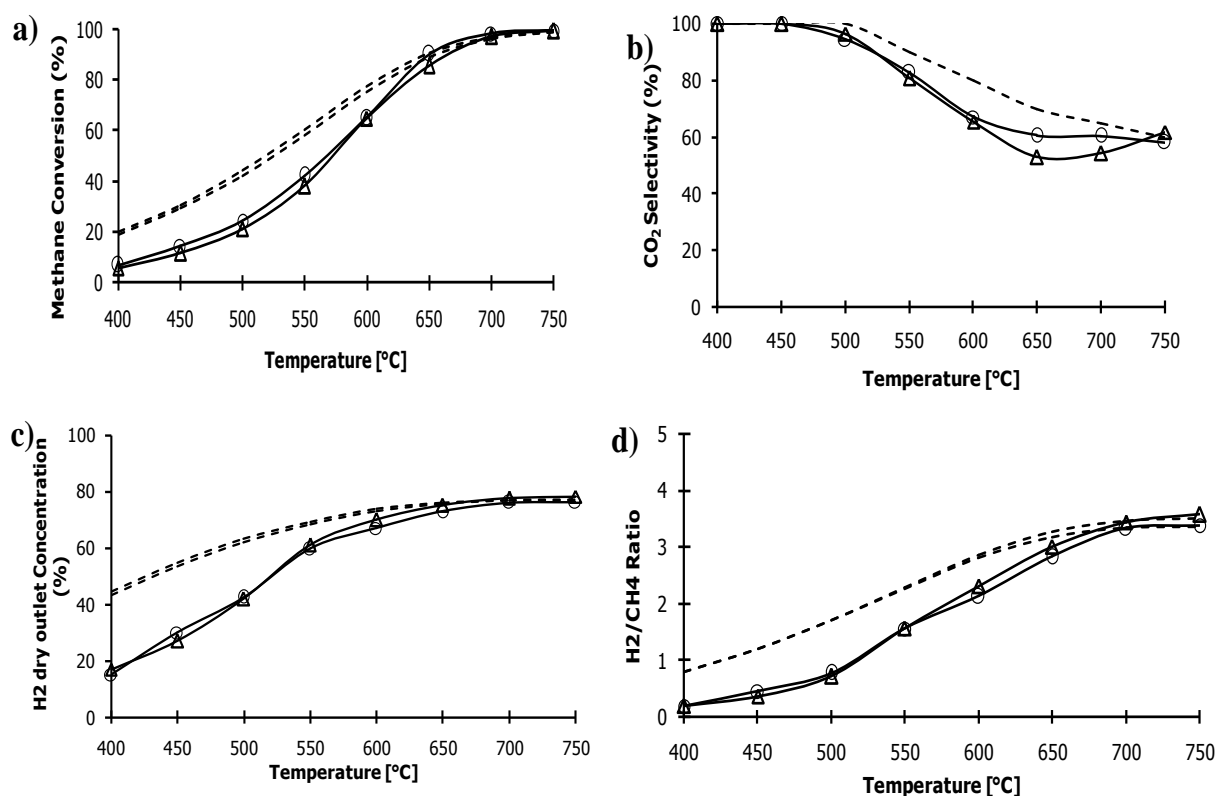


Figure 7.8: Temperature Effect on catalytic activity at WSV 20 on different S/C ratio, a) methane conversion, b) CO₂ selectivity, c) H₂ dry outlet concentration, d) H₂/CH₄. Δ = S/C 3, \circ = S/C 2.8, -- = equilibrium values

Secondly the influence of S/C ratio on catalytic activity was determined as presented in **Figure 7.8(a-d)**. The catalytic test was conducted in the temperature range of 400 to 750 °C at low WSV as Pt/CeO₂ catalyst performed better at low WSV (see **section 7.3.2.1**). The S/C ratio was varied by keeping the WSV constant at 0.33 NL·min⁻¹·g_{cat}⁻¹ and adjusting the corresponding flow rate of steam and methane.

At S/C ratio 3.2 the catalyst showed very unstable activity (figure not shown) below 600 °C, however the catalyst achieved 99% methane conversion with 74% H₂ dry outlet concentration and 47% CO₂ selectivity at 750 °C.

In general the catalyst performed better in the temperature range of 400 to 750 °C at S/C 2.8 as the values of methane conversion and H₂ dry outlet concentration remained slightly higher than at S/C 3 (see **Figure 7.8 a and c**).

At 650°C the catalyst showed 90% methane conversion with 75% H₂ dry outlet concentration at S/C 2.8, slightly higher than S/C 3 where the catalyst achieved 86% methane conversion with 75% H₂ dry outlet concentration. At 750°C the catalyst achieved 99% methane conversion at both S/C 2.8 and 3 however, the catalyst showed a little low (77%) H₂ dry outlet concentration at S/C 2.8 compared to 78% H₂ dry outlet concentration at S/C 3.

At S/C 2.8 and between temperature range of 600 and 700°C a slight increase in CO₂ selectivity values (see **Figure 7.8c**) indicate the favoring of WGS reaction. A slightly higher H₂/CH₄ ratio was observed at S/C 3 (see **Figure 7.8d**). Increasing S/C ratio increases the partial pressure of steam in the reaction mixture⁵⁴ and in case of Pt/CeO₂ low pressure favors the steam reforming reaction indicating that the catalyst is active at lower temperature.

At 700°C the catalyst was more active at S/C 2.8 as it gave higher CO₂ selectivity, so with the goal of producing pure hydrogen with higher CO₂ selectivity an ageing test with daily startup and shutdown cycle was carried out to test the stability of the catalyst.

7.3.2.3 Ageing with daily startup and shutdown cycles in N_2

environment:

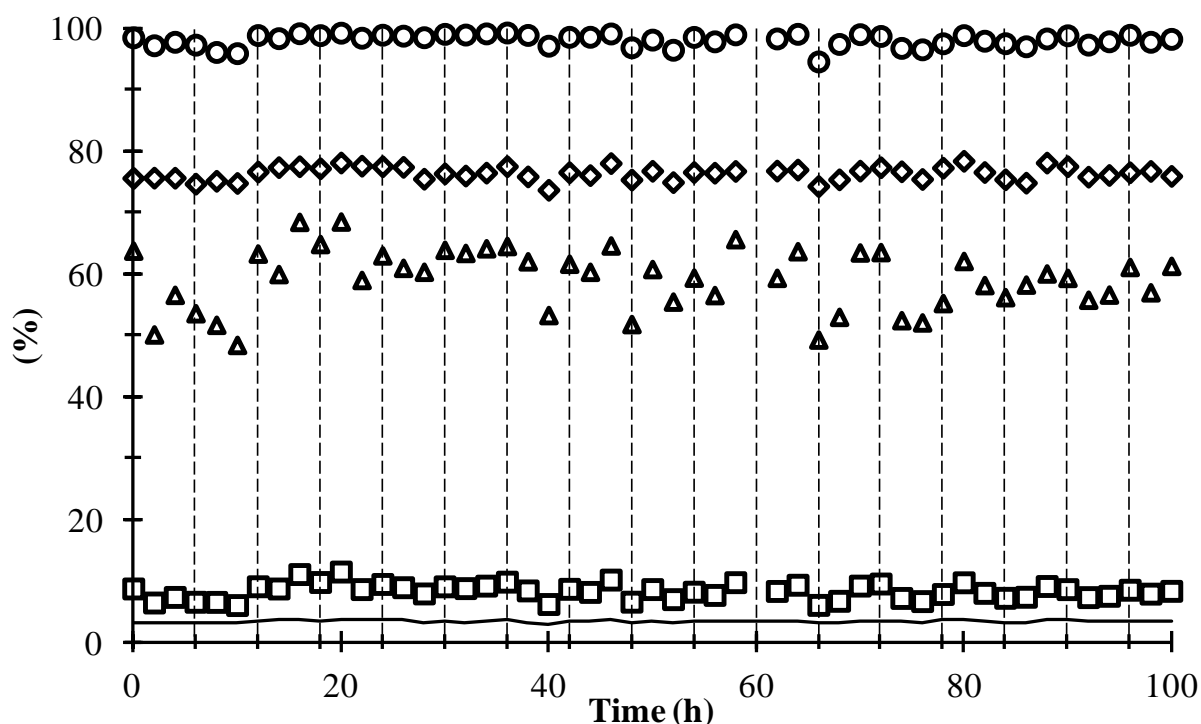


Figure 7.9: Time effect on catalytic activity of 1.13% Pt/CeO₂ catalyst at 700°C with daily startup and shut down cycle in N₂ environment. ○ = methane conversion, ◇ = H₂ dry outlet concentration △ = CO₂ selectivity □ = H₂/CO molar ratio, - = H₂/CH_{4,reacted} molar ratio

Stability test carried out with N₂ start up and shutdown cycles after about 6 h of reaction time at 700°C with S/C 2.8 and WHSV 0.33NLmin⁻¹·g_{cat}⁻¹ are reported in **Figure 7.9**. The 6h time interval is indicated by vertical dotted line on the graph. High stability during 100h of reaction was observed for Pt/CeO₂ catalyst. The methane conversion remained greater than 93%, CO₂ selectivity above 48%, CO in dry reformat maximum about 12%, CO₂/CO selectivity ratio varying between 0.8 to 2, H₂ composition higher than 75% reaching up to 80% and H₂/CO ratio varying between 6-11.5 during entire reaction time.

Another phenomenon observed during 100h ageing with inert startup and shutdown cycle is frequent and analogous oscillation behavior of methane conversion, H₂ composition and CO₂ selectivity. Change in H₂ composition (77±2%) with respect to change in methane conversion (98±2%) is almost

similar and less oscillatory but oscillation in CO_2 selectivity is rather large ($59 \pm 8\%$). This frequent oscillatory behavior can be explained through the repeated oxidation/reduction cycle occurrence at catalyst surface

The stability of Pt catalyst is high as compared to other steam reforming catalysts which show reduced catalytic activity within 5h of reaction^{14,25,37,53}. Zhai et al.⁵³ carried out MSR stability test over Ni catalyst showing methane conversion above 90% for more than 10h and decreasing to 10% in slowly in later 30h, deactivating is mainly due to sintering and coke deposition. Mortola et al.²⁵ carried out MSR over impregnated Pt catalyst and considerable catalytic activity decrease was observed within 24 h of reaction, same was observed by Pino et. al.⁴² During partial oxidation of methane when impregnated Pt sample deactivated evidently during 100 h of reaction

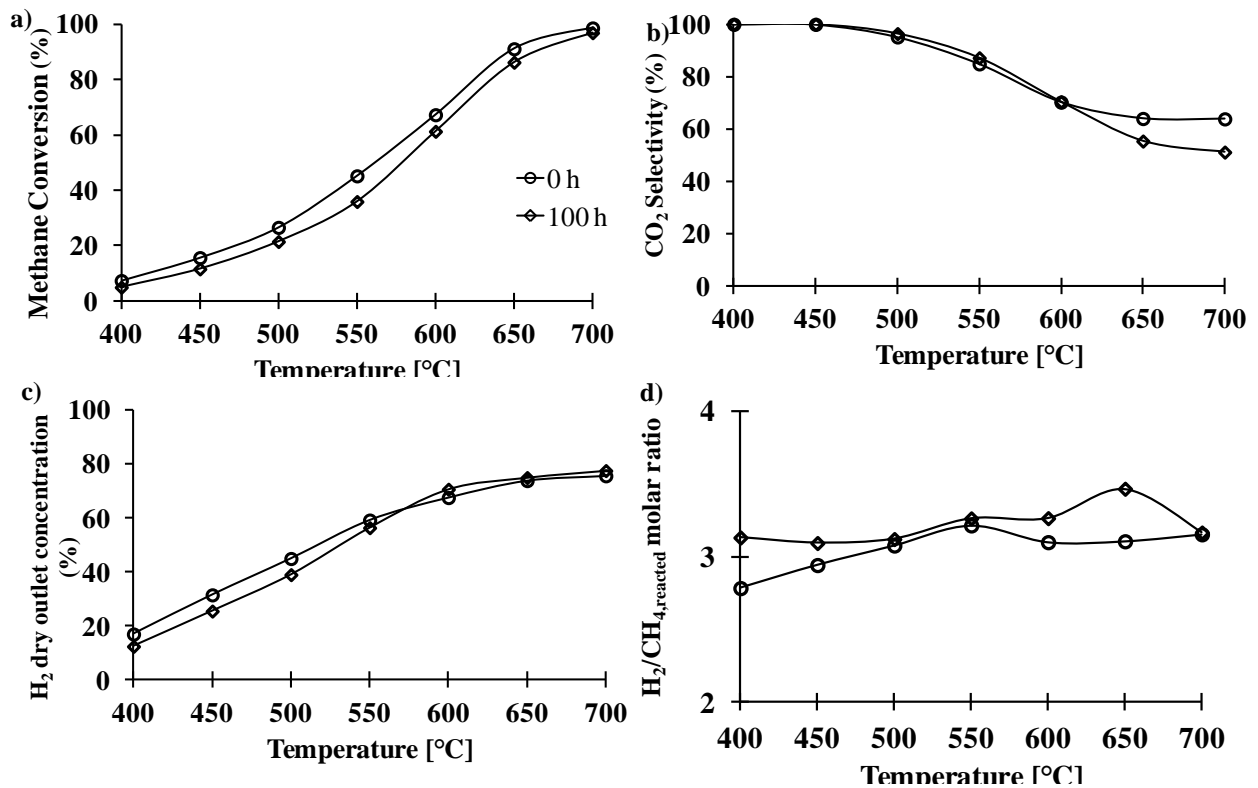


Figure 7.10: Temperature Effect on catalytic activity before and after 100h reaction time ○ = 0h, ◇ =100h

After 100h ageing test the performance of catalyst from 400 -700°C was evaluated and a comparison of the performance of the catalyst is presented in **Figure 7.10**. Decreases in the methane conversion over time is evident from the

plot for the performance at 0 and 100 h conversion remain same with a very slight change as the conversion decreases about 1% at 100h, however a 5% decrease in methane conversion is more evident at lower temperatures (see **Figure 7.10a**). For CO₂ selectivity **Figure 7.10b** the catalyst showed similar activity at and below 600°C, however 13% drop in CO₂ selectivity is observed at 650 and 700°C after 100h of reaction time. A decrease of 5% in H₂ dry outlet concentration was observed at and below 550°C; though the catalyst showed similar values from 600 to 700°C. The H₂/CH_{4,reacted} molar ratio improved after 100h of reaction time.

7.3.2.4 Ageing with daily startup and shutdown cycles in reaction

Environment:

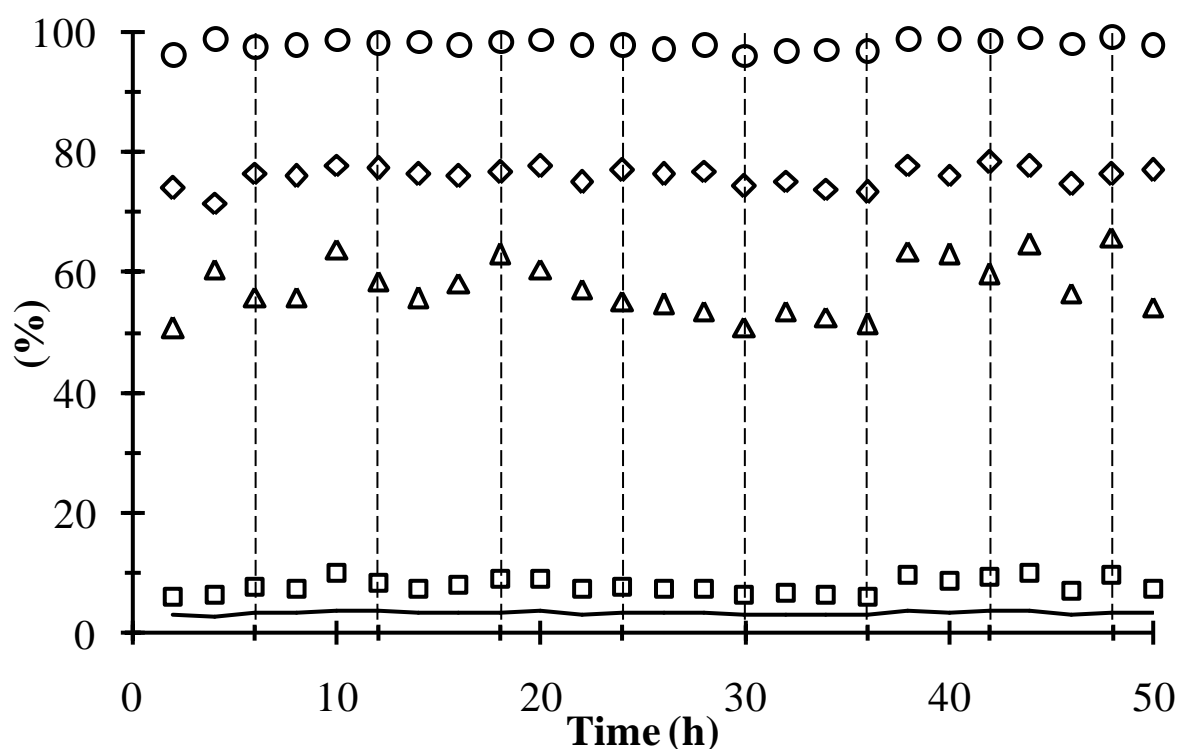


Figure 7.11: Time effect on catalytic activity of 1.13% Pt/CeO₂ catalyst at 700°C with daily startup and shut down cycle in reaction environment. ○ = methane conversion, ◇ = H₂ dry outlet concentration △ = CO₂ selectivity □ = H₂/CO molar ratio, - = H₂/CH_{4,reacted} molar ratio

After stability test with daily start up and shutdown cycle N₂ environment, endurance test was carried out in daily start up and shut down cycle in the

reaction environment at 700°C with S/C ratio 2.8 WHSV $0.33 \text{ NL min}^{-1} \text{ g}_{\text{cat}}^{-1}$ as presented in **Figure 7.11**. The daily start up and shut down in the reaction environment was to evaluate the effect of heating and cooling in reaction environment on the catalytic activity. High stability during 50h of reaction was shown for Pt/CeO₂ catalyst. The methane conversion remained more than 96%, CO₂ selectivity above 48%, CO in dry reformat maximum about 12%, CO₂/CO selectivity ratio varying between 0.9 to 1.7, H₂ composition higher than 73% up to 80% and H₂/CO ratio varying between 6-10 during all the reaction time

Same oscillatory trend is observed in 50h ageing in reaction environment startup and shutdown cycle but less frequent. Comparison of ageing during inert and reaction environment shows no significant difference. Average methane conversion and composition of H₂ and CO₂ remains same for both environments showing that ageing is insensitive to cyclic environmental change

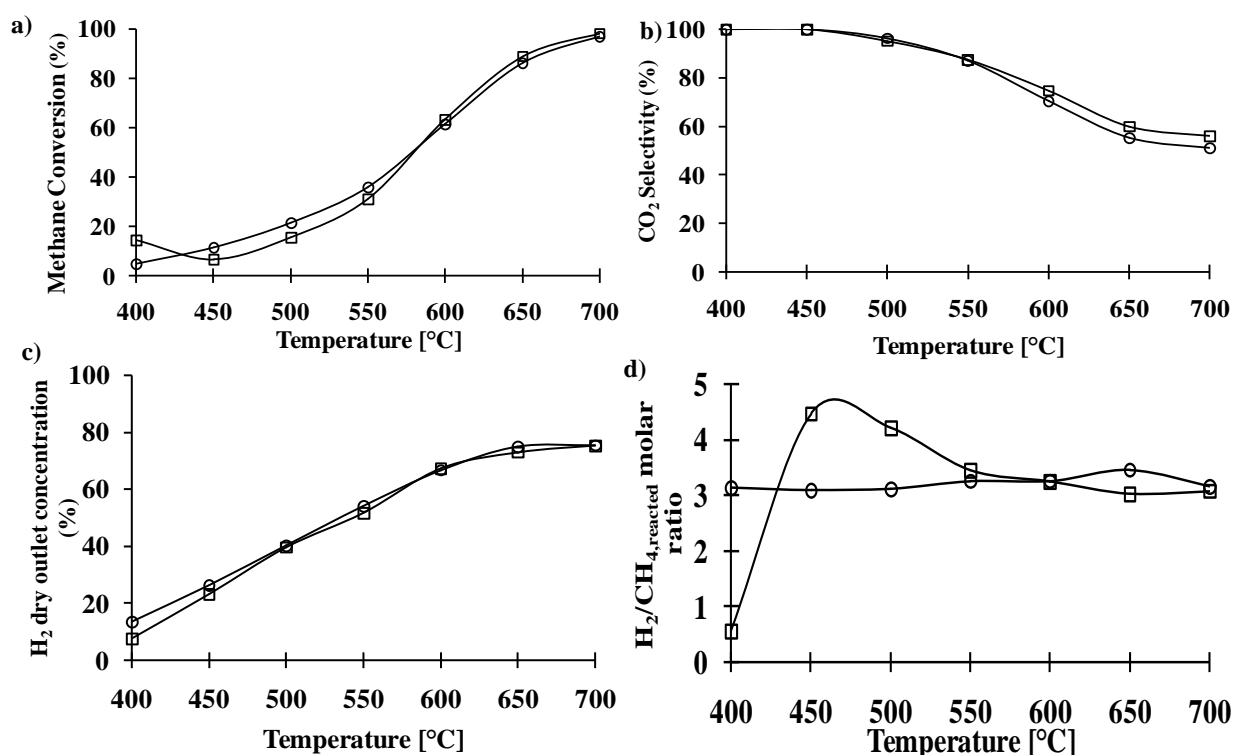


Figure 7.12: Temperature Effect on catalytic activity before and after 50h

reaction time at 700°C, ○ = 100h, □ = 150h

After performing ageing test with daily start up and shut down cycles in the reaction environment, the performance of catalyst from 400 to 700°C was evaluated as presented in **Figure 7.12**. A 5% decreases in the methane conversion at and below 550°C is evident from the plot for the performance at 100 and 150 h. The trend however remain the same and at temperature above 550°C the conversion remain same with a very slight change as the conversion decreases about 1%. A slight increase in CO₂ selectivity of 5% is observed at about 700°C, however the CO₂ selectivity remained unchanged below 550°C. H₂ dry outlet concentration showed negligible difference however H₂/CH₄ molar ratio improved over time.

7.3.3 Aged Catalyst Characterization:

7.3.3.1 TEM:

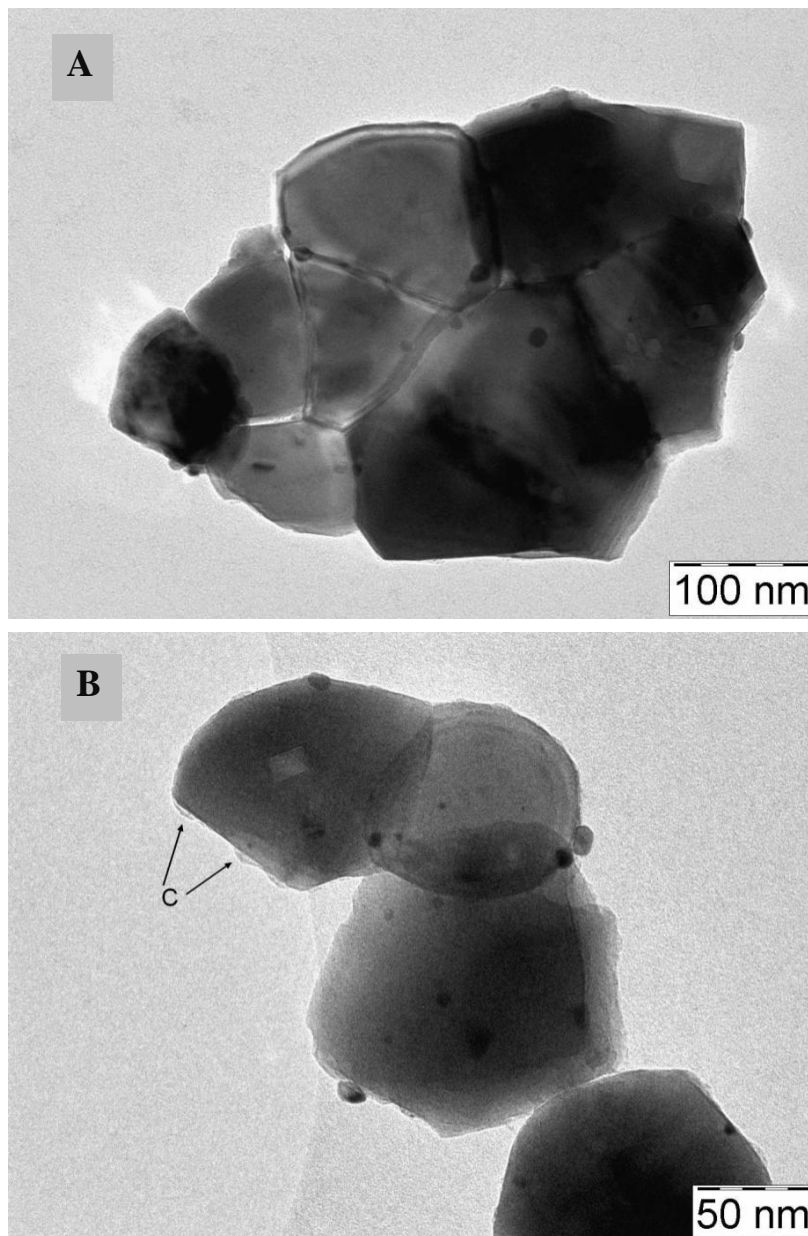


Figure 7.13: TEM image of catalyst after 150 h of ageing

Aged catalyst TEM is shown in **Figure 7.13**. A very thin layer of carbon is visible on catalyst surface with a slight change in Pt particle size indicating some degree of sintering.

7.3.3.2 XRD

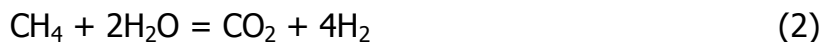
XRD pattern of aged catalyst (not shown) the CeO_2 phase is visible with less intensity and lower 2θ shift than the original fresh catalyst and no Pt peaks are visible. The lower 2θ shift can be due to thermal defects generated within the system.

7.3.3.3 XPS

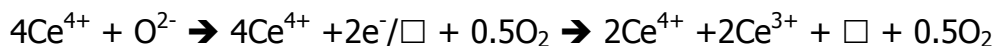
The XPS spectra of used catalyst is shown in **Figure 7.4-Figure 7.6**. The peaks of Ce 3d core level region are fitted as before **Figure 7.4a**. The surface concentration of Ce^{3+} of total Ce (**Table 7.2**) on used sample is slightly higher than the fresh sample. This is mainly due to during H_2 reduction Ce^{3+} concentration increases along with the chemisorbed oxygen O_H which are highly reactive species³⁶ therefore, high catalytic activity is due to in time supplemented oxygen vacancies. XPS study shows ratio of 1.6 of Carbon on spent catalyst to that on fresh catalyst and this value is somewhat very low compared to other situations¹⁴. The Pt peaks shift towards low B.E was observed due to decomposition of PtO which resulted in increase of Pt^0 state on the catalyst during reduction as indicated in **Table 7.2**. Moreover, surface atomic ratio of Pt/Ce decreased from 0.07 to 0.01 indicating decrease in Pt at surface due to sintering and carbon coverage of Pt particles as indicated by TEM and XRD analysis.

Despite some degree of sintering and thin layered carbon coverage on catalyst, as shown by TEM, XPS and XRD, the catalyst remained active after 150h of reaction. This highly stability of Pt/ CeO_2 can be attributed to combination of Pt and Ce^{56} which creates $\text{Pt}^0/\text{Pt}^{\delta+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples giving increased methane conversion and carbon resistance over Pt catalyst²⁵. So during the whole reaction the oxygen specie formed from lattice oxygen at CeO_2 /soot interface and is enhanced by deposition of noble metal over CeO_2 ⁵⁷. Redox coupling of Pt and Ce is responsible for decreased coking. Sintering of Pt particles is due to high temperature reaction and weakening of Pt-O-Ce bond.

Among 11 possible steam reforming reactions⁵⁷ CO₂ can only be produced through following three reactions.



The first reaction (1) corresponds to the water gas shift reaction in which 1 mole of CO, produced through MSR reaction, is converted to CO₂. Secondly water gas shift reaction which in presence of Pt/CeO₂ is enhanced even higher temperature^{50,51} and quickly approaches equilibrium. If WGS reaction reaches equilibrium then the CO₂/CO selectivity ratio should be equal to 1, but in our reaction system this ratio exceeds 1 therefore it means CO is not solely converting to CO₂ by means of water gas shift but also through reaction with lattice oxygen. Lattice oxygen can be produced via the transformation of Ce³⁺ and Ce⁴⁺ through following equations^{47,58}



The deposition of Pt metal on CeO₂ having strong metal surface interaction changes the surface electronic state thus increasing Ce³⁺ concentration and the higher the concentration of Ce³⁺ concentration of the total Ce, the more oxygen vacancies form. The deposition of Pt metal weakens the bond energy between Pt metal and oxygen atom close to Pt metal in CeO₂ crystal lattice which makes this kind of oxygen atom more easily reducible so number of oxygen vacancies increases⁵⁹. So with the MSR and water gas shift the change in product composition should be constant but it seems that CO reaction with the lattice oxygen, produced by oxidation/reduction behavior of catalyst is responsible for the oscillation of CO₂ in system.

Second reaction (2) however yields CO₂ along with 4moles of H₂ per mole of CH₄ reacted. As during the whole reaction time (150h) the ratio of H₂ per mole of CH₄

reacted remained greater than 3 therefore the second reaction seems more dominating.

Third reaction (3) involves the dissociation of CO which yields carbon and CO₂ known as Boudouard reaction. Theoretically for Boudouard reaction/disproportionation reaction of CO the ratio of CO/CO₂ should be almost 2 but results show that this ratio is less than 1 for our system and also from TEM results there is a very thin layer of carbon on catalyst surface so if carbon is deposited through Boudouard reaction its effect is very small and insignificant.

7.4 References

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Chapter 8 Rh/CeO₂ catalyst for methane steam reforming: Catalytic activity and stability

8.1 Introduction

Global warming increase and depleting oil reservoirs call for an alternative environmental friendly energy resource. Hydrogen due to its high energy content and zero emission after combustion can potentially replace the conventional fuels¹⁻³. Hydrogen production on a small scale is the major shortcoming in this scenario. Commercially hydrogen is produced along with CO and CO₂ from methane via steam reforming reaction^{1,4}. According to US department of energy the MSR can provide an initial step towards hydrogen economy.

Steam reforming is an endothermic process and thus requires a high energy input. MSR is preferred among other technologies like partial oxidation, autothermal reforming, oxidative steam reforming and coal gasification⁵ due to its energy efficiency (83%) with lowest hydrogen cost. Steam reforming also provides excellent H₂ concentration with good fuel processor efficiency⁶. Commercially Ni is used as a catalyst for MSR but the issues of sintering and carbon deposition are high on Ni catalyst. Also ageing reduces the porosity and Ni content therefore deactivating the catalyst and results in increase in operating temperature and pressure⁷. Noble metals are potential alternative for Ni in the MSR reaction, as the amount of Ni varies from 10% on commercial catalyst⁸⁻¹² while a small amount of noble metal can produce even better results¹³ and remain active for long time period.

Noble metals like Rh¹⁴⁻¹⁷, Pt¹⁸⁻²⁷, Ru²⁸⁻³², Pd³³⁻³⁵ and Ir^{36,37} have been widely studied for methane steam reforming. There is a constant debate regarding order of activity among noble metals³⁸ and Rh and Ru are considered to be most

active, and Rh gives the highest affinity among noble metals with CeO_2 ³⁹. According to study conducted by Wei and Iglesia⁴⁰ Rh is active among noble metals for the activation of C-H bond during reforming reaction. Wang et al⁴¹ the decrease of electron density of Rh facilitates the activation and dissociation of CH_4 .

Usually Noble metals are supported on inert supports like Al_2O_3 , but CeO_2 supported noble metals are being considered due to oxygen storage capacity, strong metal support interaction^{42,43}, soot resistance⁴⁴ and the CeO_2 reducibility⁴⁵ ($\text{Ce}^{4+}/\text{Ce}^{3+}$). These properties of CeO_2 helps in determining a higher specific rate of the supported noble metals, compared to the usual inert oxide supported catalysts, particularly in reactions such as water gas shift, steam reforming and dry reforming of methane. According to the J. Xu et.al.⁴⁶, the CeO_x ($x = 2$ or 1.5) accelerate the reaction of steam with adsorbed carbon species on the metal surface at the metal–oxide interface, so, the surface carbon species can be quickly converted to gaseous products, preventing accumulation due to the ceria capacity of remove deposited carbon species via gasification by the O species supplemented from the lattice oxygen of the catalyst itself.

Rh/ CeO_2 catalyst has been extensively studied for CO oxidation⁴⁵, oxidative methane steam reforming⁴⁷. Wang et. al.¹⁶ carried out methane reforming over Rh/ CeO_2 - Al_2O_3 and evaluated the role of $\text{Rh}^0/\text{Rh}^{\delta+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples which generate electron deficient Rh and Ce promoting CH_4 and CO_2 activation and enhancement of carbon elimination to yield CO over Rh catalyst.

In this work a Rh catalyst supported on a CeO_2 carrier was synthesized, characterized and tested towards MSR reaction. Moreover the stability of the catalyst was also evaluated by 100h endurance test. The performance of the catalyst in cyclic condition during daily startup and shutdown cycle was also evaluated.

8.2 Experimental

8.2.1 Catalysts preparations

1.5% Rh/CeO₂ was prepared by IWI method. CeO₂ carrier was prepared by solution combustion synthesis (SCS). Metal nitrate precursor of Ce i.e. Ce(NO₃)₃*6H₂O and urea (CH₄N₂O) as fuel were placed together in aqueous solution and heated up to 600°C in a furnace. The reaction resulted in formation of CeO₂ powder. The so synthesized powder was then calcined for 3h at 650°C. Rh was deposited by incipient wetness impregnation method, an aqueous solution of RhCl₃ was prepared and deposited drop wise on support, meanwhile thoroughly mixing the whole mass at 130°C in order to let water evaporate.

The prepared catalyst was calcined in air at 800°C for 3 h.

8.2.2 Catalytic Activity

The catalytic activity of the catalyst was evaluated in temperature range of 400-750°C. Also stability under DSS_{inert} conditions and 100h continuous ageing of the catalyst was performed. Details of catalytic activity measurements, stability tests and kinetic measurements are presented in **Chapter 2**.

8.2.3 Catalysts Characterization:

The catalyst prepared were characterized by CO Chemisorption, Porosimetry, Density, XRD, SEM EDX and XPS analysis

8.3 Results and Discussion

The physical characteristics of as prepared catalyst are presented in **Table 8.1** .

Table 8.1: Physical Properties of the fresh catalyst

Average pellet size	300 µm
BET Surface Area	2 m ² /g
Rh Content -ICP	0.24 %

Skeletal Density	6.96 g/cm ²
Geometric density	1.93 g/cm ²
Pore Volume	0.015 cm ³ /g
Porosity	0.72 cm ³ /cm ³
Pore diameter of catalyst	32.3 nm

The Rh/CeO₂ catalyst showed a surface area of 2m²/g, very low than the other Rh catalysts available in literature. CeO₂ showed a surface area of 66.25m²/g and addition of Rh decreased the surface area significantly. ICP reveals 0.24% of Rh on CeO₂.

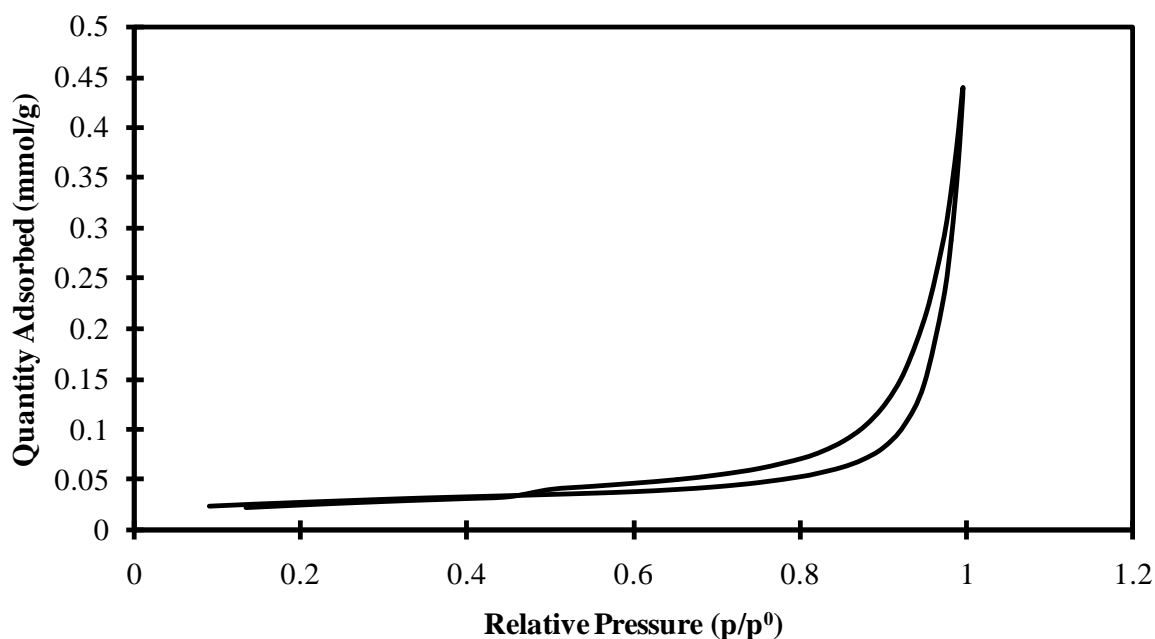


Figure 8.1: Porosimetry of as prepare Rh/CeO₂ catalyst

The N₂ adsorption isotherm obtained is shown in **Figure 8.1**. The catalyst showed a type IV isotherm with a type H3 hysteresis loop at the high relative pressure range. The type IV isotherm is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high relative pressure. The shapes of hysteresis loops have often been identified with specific pore structures. Thus, the type H3 is often associated with the aggregates of plate like particles giving rise to slit shaped pores⁴⁸.

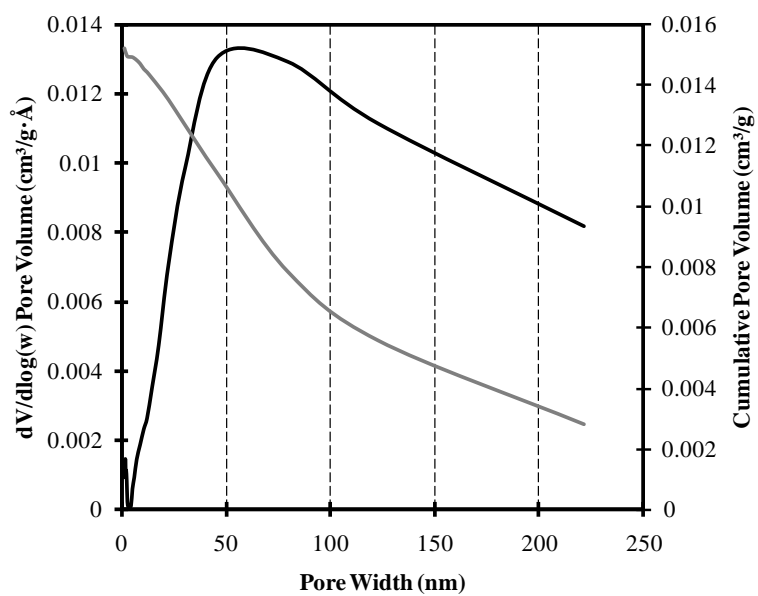


Figure 8.2: BJH pore size distribution of as prepared Rh/CeO₂

Figure 8.2 show the BJH pore distribution of Rh/CeO₂ catalyst. Most of the pores are in the range between 10-80nm.

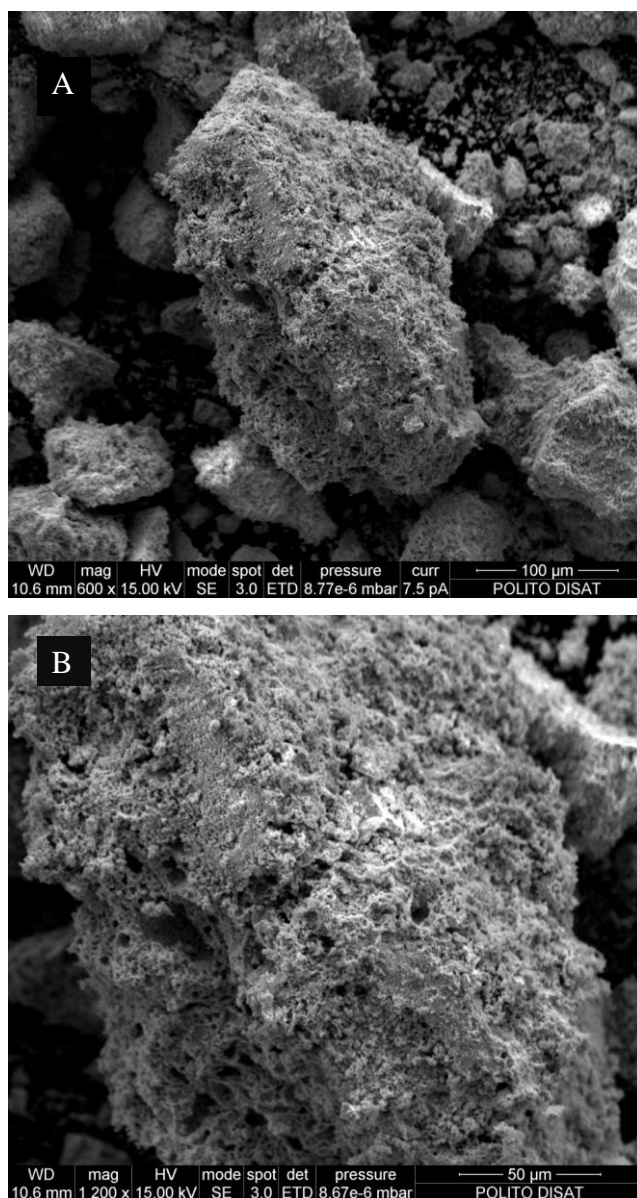


Figure 8.3: SEM micrograph of as prepared Rh/CeO₂ catalyst

The morphology of as prepared catalyst is shown by SEM micrograph in **Figure 8.3**. The catalyst shows a porous and integrated structure. Plate like particles are also visible all over the catalyst surface as determined from Porosimetry.

8.3.1 XRD

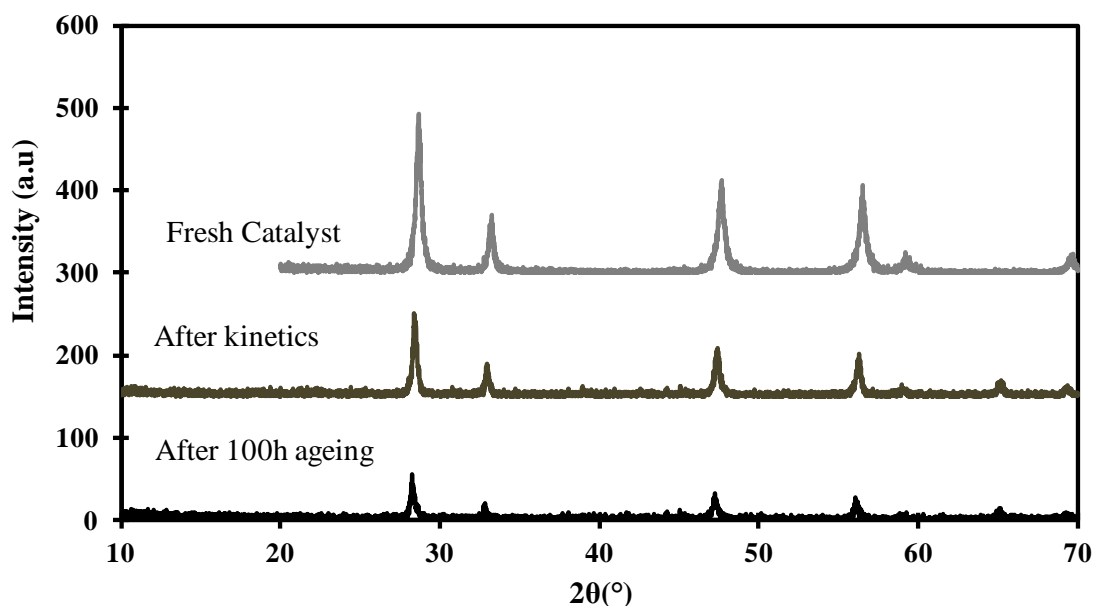


Figure 8.4: XRD pattern of as prepared Rh/CeO₂ catalyst

XRD pattern of as prepared Rh/CeO₂ **Figure 8.4** was recorded to check the presence of Rh metal or its oxide phases. XRD pattern corresponds to fluorite CeO₂ phase⁴⁹ ($2\theta = 28.67^\circ, 33.26^\circ, 47.68^\circ, 56.58^\circ, 59.23^\circ$) and diffraction lines due to Rh₂O₃, RhO₂ and Rh metal could not be detected. It shows that Rh metal is well dispersed on CeO₂. The related CeO₂ particle size, derived from Ce (111) peak by application of the Scherrer equation is 372 nm. Slight shift of CeO₂ peaks to higher degrees compared to pure CeO₂ (JCPDS card no 81-0792, $2\theta = 28.54^\circ, 33.07^\circ, 47.47^\circ, 56.33^\circ, 59.07^\circ$ and 69.401°) indicate the formation of oxide solid solution²⁷. The related cell parameter of prepared catalyst results $a = 5.3975 \text{ \AA}$ which is slightly smaller than pure CeO₂ ($a = 5.4124 \text{ \AA}$). The shrinkage in lattice parameter can be due to replacement of Ce⁴⁺ (ionic radius = 0.97 \AA) by Rh³⁺ (0.665 \AA) and Rh⁴⁺ (0.6 \AA).

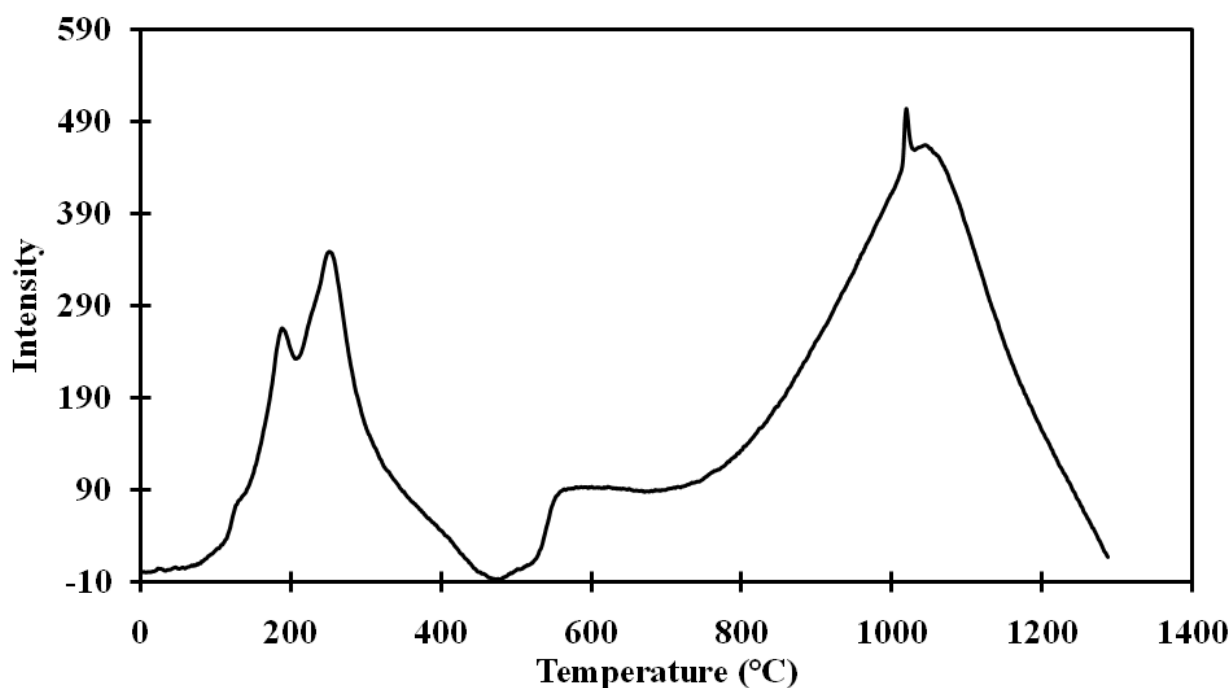


Figure 8.5: Temperature Programmed Reduction (TPR) profile of as prepared Rh/CeO₂ catalyst

TPR profile of Rh/CeO₂ catalyst presented in **Figure 8.5** depicts two peaks the first peak is low temperature peak corresponding to the surface reduction of the material while the second high temperature peak corresponds to the bulk reduction of solids¹⁶. A twin peak centered at 185°C and 251°C corresponds to reduction of Rh₂O₃ to Rh⁰ state⁴⁵. The peak at 185°C is related to reduction of well dispersed small Rh particles while at 251°C the large Rh₂O₃ crystals are reduced⁴⁵. The second peak around 1018°C corresponds to the bulk reduction of CeO₂ to Ce₂O₃¹⁶.

The surface atomic composition obtained from XPS along with SEM EDX results is presented in **Table 8.2**. Atomic percent obtained from SEM EDX are higher compared to XPS results.

Table 8.2: Surface atomic composition from XPS and EDX

Samples	Surface Atomic %			Ratio	EDX
	Ce	O	Rh	Rh/Ce	Rh

Fresh (0 h)	10.2	45.3	0.4	0.039	1.07
After 100h ageing	3.4	59	0.1	0.029	-
After Kinetic Analysis	4.8	38.2	0.1	0.02	-

Ce (3d) peaks in B.E range 875-925 eV of as prepared catalyst are presented in **Figure 8.6**. The Ce 3d spectrum consists of eight peaks which corresponds to four pairs of spin orbitals doublets. Ce ($3d_{5/2,3/2}$) peaks at 882.6 and 900.93 eV with characteristic satellite marks (see **Figure 8.6**) corresponds to CeO₂ with Ce in +4 oxidation state.

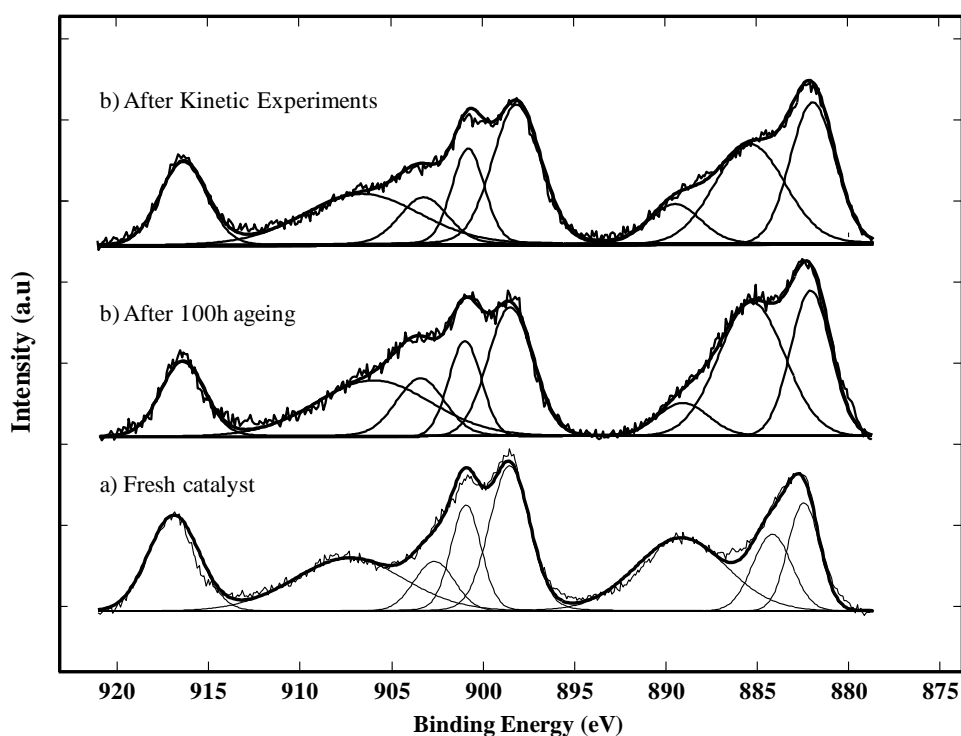


Figure 8.6: Ce 3d spectra of Rh/CeO₂ catalyst

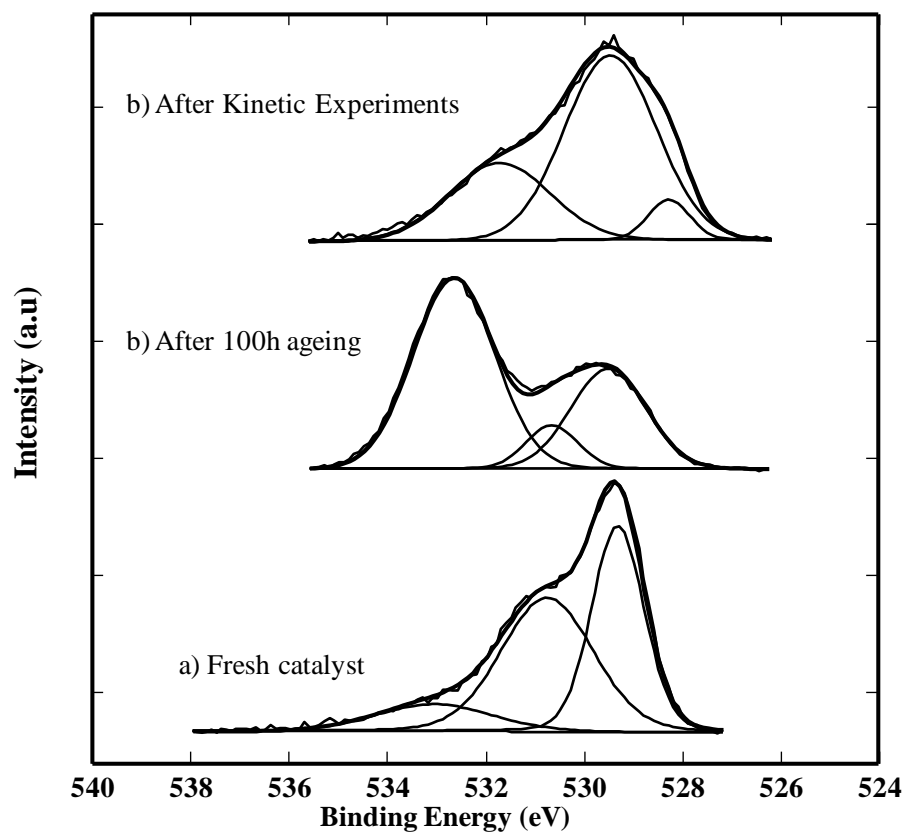


Figure 8.7: O1s spectra of Rh/CeO₂ catalyst

XPS profile of O1s **Figure 8.7** exhibits three binding energies at 529.27 eV, 530.77 eV and 532 eV. The first binding energy represents the surface lattice oxygen (O_L) while the second represents oxygen due to Rh oxidation and the third binding energy represents chemisorbed surface oxygen (O_H) which only makes up 12% of total oxygen. Higher O_H concentration verifies the rich presence of chemisorbed surface oxygen species that generally act as the most reactive oxygen species⁵⁰

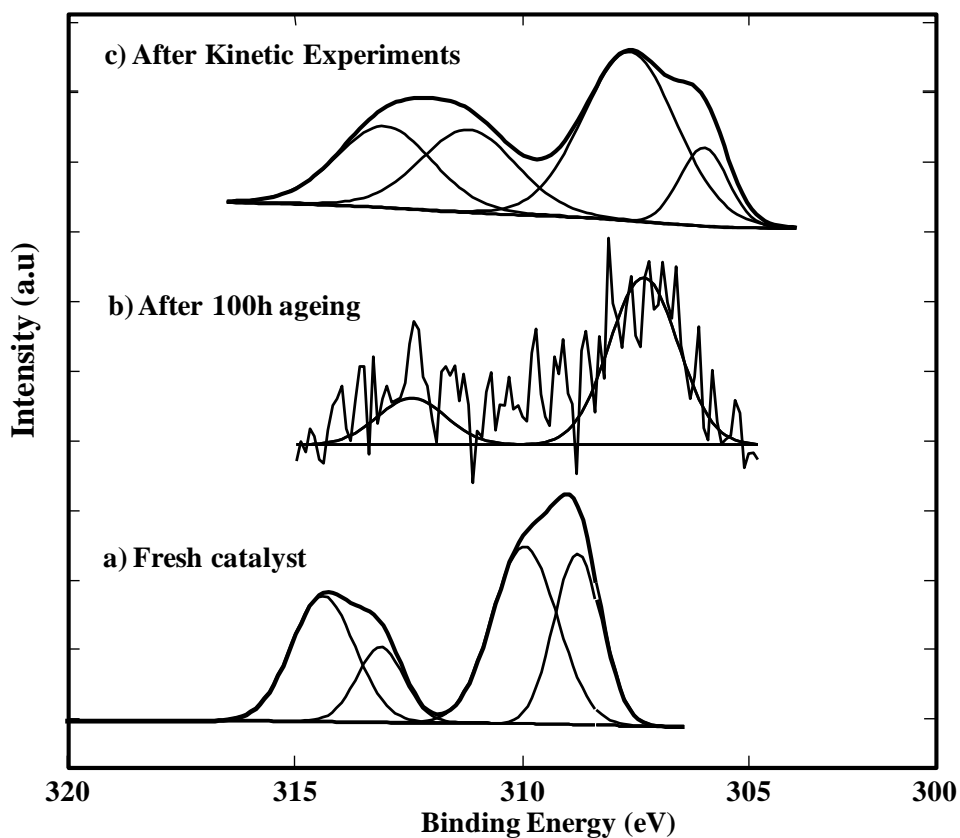


Figure 8.8: Rh 3d spectra of Rh/CeO₂ catalyst

Rh 3d spectra **Figure 8.8** has been resolved in two sets of spin orbital doublets. The Rh⁰ shows 3d_{5/2} BE at 307.1eV while the Rh³⁺ shows 3d_{5/2} BE at 308.8 eV. For CeO₂ promoted Rh catalyst the Rh 3d_{5/2} and 3d_{3/2} peaks moved to 308.75eV and 313.08eV respectively. The 3d_{5/2} peak electropositive shift at 308.75eV indicates a transition between Rh⁰ and Rh³⁺, thus generating Rh⁰/Rh^{δ+} redox couple.

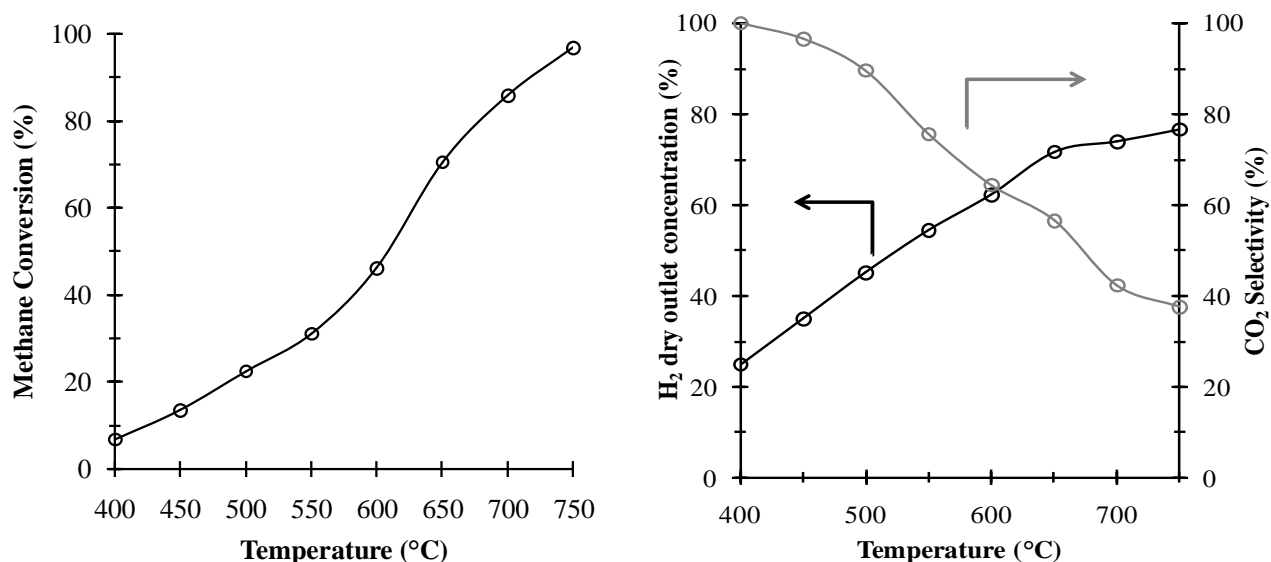


Figure 8.9: Temperature Effect on (A) Methane Conversion, (B) H₂ dry outlet concentration and CO₂ selectivity for 1.5% Rh/CeO₂ S/C:3, W/F_{CH₄}=16128 kg_{cat}⁻¹ h⁻¹ kmol⁻¹, P_T=1bar

Effect of temperature on methane conversion at 1 atm pressure and S/C ratio 3 is presented in **Figure 8.9**. Methane conversion increases gradually with temperature starting from 7% at 400°C reaching 98% conversion at 750°C. The methane conversion of Rh at 750°C is higher and comparable to 3% Rh catalyst and higher than 10%Ni catalyst, although our space velocity is half of Kusakabe et al¹³ and double than Zhai et.al.⁵¹

At 750°C the CO₂ selectivity drops down to 38% with H₂/CO molar ratio 5.41 and catalyst showed an increase in H₂ dry outlet concentration achieving up to 77%. The methane conversion, H₂ dry outlet concentration and CO₂ selectivity values remain lower than the equilibrium values.

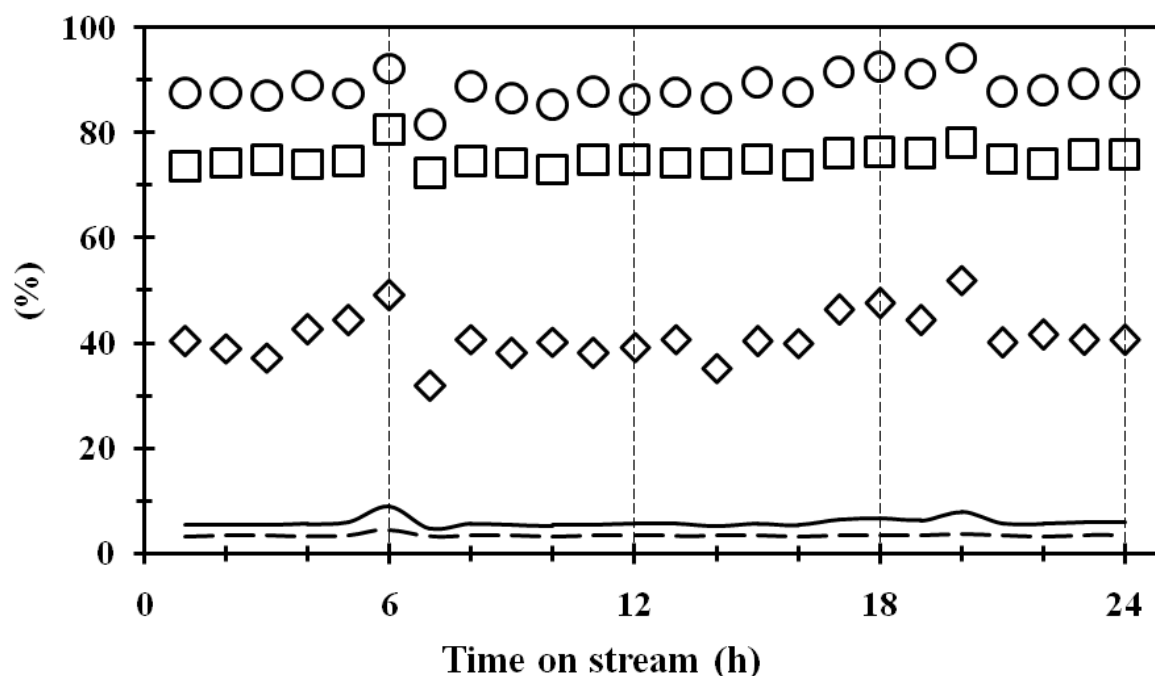


Figure 8.10: Time effect on catalytic activity of Rh/CeO₂ catalyst at 700°C with daily startup and shut down cycle in N₂ environment at $P_T = 1\text{ bar}$, $S/C: 3$ and $W/F_{CH_4} = 16128 \text{ kg}_{cat}\cdot\text{h}^{-1}\cdot\text{kmol}^{-1}$. \circ = methane conversion, \square = H₂ dry outlet concentration \diamond = CO₂ selectivity, — = H₂/CO molar ratio, ---- = H₂/CH_{4,reacted} molar ratio

Secondly catalyst was aged at 700°C for 25h to determine whether the catalyst is stable enough for kinetic tests. **Figure 8.10** The catalyst showed a stable activity over 25h time period with regular startup and shut down cycle indicated by the dotted lines. High stability during 25h of reaction was observed for Rh/CeO₂ catalyst. The average methane conversion over 25h time was 88%, CO₂ selectivity above 30%, H₂ composition higher than 70% reaching up to 80% and H₂/CO ratio varying between 4.7-8.8 during entire reaction time.

Another phenomenon observed during 25h ageing with daily startup and shutdown cycle is frequent and analogous oscillation behavior of methane conversion, H₂ composition and CO₂ selectivity. Change in H₂ composition (75±4%) with respect to change in methane conversion (88±6%) is almost similar and less oscillatory but oscillation in CO₂ selectivity is rather large (41±10%). The catalyst showed an oscillatory behavior which can be attributed to structural parameters of catalyst. This frequent oscillatory behavior of CO₂ can be explained through the repeated oxidation/reduction cycle occurrence at

catalyst surface generating $\text{Rh}^0/\text{Rh}^{\delta+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couples^{16,41,45}. Now when the Ce^{3+} is active the CO_2 undergoes dissociation on the support surface thus responsible to increase in CO in the product stream. However when Ce^{4+} is dominant the CO concentration decreases in the dry reformat. The catalyst showed no deactivation over 25h time period.

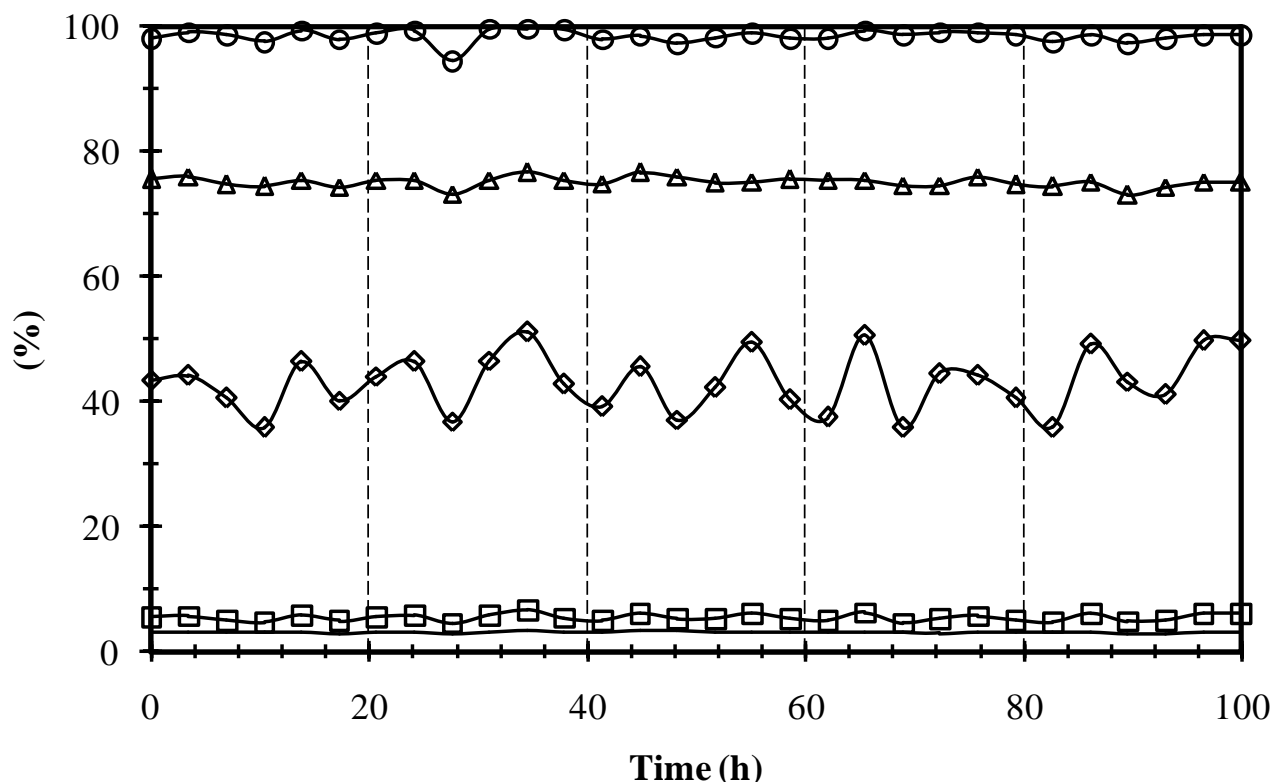


Figure 8.11: Time effect on catalytic activity of Rh/CeO₂ catalyst at 750°C for 100h $P_T = 1\text{bar}$, $S/C: 3$ and $W/F_{\text{CH}_4} = 16128 \text{ kg}_{\text{cat}}\cdot\text{h}^{-1}\cdot\text{kmol}^{-1}$. \circ = methane conversion, \square = H_2 dry outlet concentration \diamond = CO_2 selectivity, — = H_2/CO molar ratio, ---- = $\text{H}_2/\text{CH}_{4,\text{reacted}}$ molar ratio

Thirdly the catalyst was aged at 750°C for 100h **Figure 8.11** to determine whether the catalyst is stable enough for smooth continuous operation. The catalyst showed a stable activity over continuous 100h time period. High stability during 100h of continuous reaction time was observed for Rh/CeO₂ catalyst. The methane conversion remained constant at 98%, H_2 composition higher than 73% reaching up to 76% and H_2/CO ratio varying between 4.58-6.72 during entire reaction time.

Another phenomenon observed during 100h ageing is frequent and analogous oscillation behavior of CO₂ selectivity. Change in H₂ composition (77±2%) with respect to change in methane conversion (98±2%) is almost similar and less oscillatory but oscillation in CO₂ selectivity is rather small (59±8%) than the daily start up and shut down cycle. This frequent oscillatory behavior can be explained through the repeated oxidation/reduction cycle occurrence at catalyst surface.

XRD pattern of aged catalyst is shown in **Figure 8.4b**. The CeO₂ phase is visible with considerably less intensity and lower 2θ shift than the original fresh catalyst and no Rh peaks are visible. The lower 2θ shift can be due to thermal defects generated within the system. However No peak due to carbon was visible in the XRD diffractogram. In the catalyst after 100h ageing XRD pattern show less intense peaks than fresh catalyst and the peaks also corresponds to fluorite CeO₂ phase⁴⁹ (2θ = 28.23°, 32.78°, 47.2205°, 56.077°, 58.878°) but with a negative shift of 2θ. This negative shift can be due to defects generated within the system after prolonged heat exposure. Also the diffraction lines due to Rh₂O₃, RhO₂ and Rh metal could not be detected indicating the lack of particle sintering. The CeO₂ crystallite size calculated from the Ce(111) peak using Scherrer equation resulted in 58.5nm smaller than the fresh sample. The related cell parameter of aged catalyst results a= 5.474 Å which is slightly higher than pure CeO₂ (a = 5.4124 Å). This expansion in lattice parameter can be due to formation of oxygen vacancies resulted by reduction of Ce⁴⁺ to Ce³⁺.

The XPS spectrum of the aged catalyst is shown in **Figure 8.6**. the peaks of Ce 3d core level region are fitted as before. The surface concentration of Ce³⁺ of total Ce (**Figure 8.6**) on aged sample is slightly higher than the fresh sample. This is mainly due to during H₂ reduction Ce³⁺ concentration increases along with the chemisorbed oxygen OH which are highly reactive species³⁶ therefore, high catalytic activity is due to in time supplemented oxygen vacancies. The Rh peaks shift towards low B.E was observed due to decomposition of Rh₂O₃ during reduction as indicated in **Figure 8.8**. Moreover, surface atomic ratio of Rh/Ce decreased from 0.03 to 0.026 indicating decrease in Rh at surface (**Table 8.2**).

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Part III: Intrinsic Kinetics

In the third and final part of this thesis, after evaluating the catalytic endurance the intrinsic kinetics of Rh/CeO₂ was evaluated. Part III consists of **Chapter 9** and comprises of the kinetic study of Rh/CeO₂.

Chapter 9 Intrinsic kinetics of Rh/CeO₂ catalyst for methane steam reforming:

In this work a Rh catalyst supported on a CeO₂ carrier was synthesized, characterized and tested towards MSR reaction. Moreover the stability of the catalyst was also evaluated by 100h endurance test. The performance of the catalyst in cyclic condition during daily startup and shutdown cycle was also evaluated.

9.1 Experimental

9.1.1 Preliminary experiments:

For kinetic measurements firstly the run consisting of catalytic activity of as prepared catalyst was made to ensure the catalytic activity. After that the same catalyst was aged for 20 h at 700°C to observe any catalytic deactivation. As there was no deactivation observed the catalyst was put through the kinetic test. For the kinetics the catalyst was heated to the desired temperature and after reaching isothermal conditions S/C ratio was varied to see the effect of methane and steam partial pressure on methane conversion, keeping WHSV constant. After this another set of experiment was conducted keeping S/C ratio constant at 3 and changing the space velocity. No inert was used in the experiments and no hydrogen was added in the feed as there was no visible catalyst deactivation.

9.2 Results and Discussion

9.2.1 Heat and Mass Transfer Limitations

To ensure that catalyst is well in the intrinsic kinetic region, internal and external mass transfer limitations were checked experimentally and theoretically. For

every data point obtained the heat and mass transfer limitations were theoretically check to further ensure kinetic controlled operation.

9.2.1.1 Interparticle Mass Transfer Limitations

For experimental determination of interparticle mass transfer limitations the methane conversion is measured at 600°C and 1atm using different pellet sizes of the catalyst. The pellet sizes used were 600µm, 425µm, 250µm, 63µm and 45µm. Gas composition consisted of S/C 3 and constant WHSV of 0.33NL/g_{cat}-min. The methane conversion does not change for pellet size below 250µm.

For theoretical calculation of interparticle mass transfer limitations, following Weisz-Prater Criteria was used.

$$C_{WP} = \frac{R_A^{obs} \rho_c R^2}{D_{A,eff} C_{As}} < 1$$

9.2.1.2 External Mass Transfer Limitations

To determine experimentally whether external mass transfer is dominant, the methane conversion is measured using different volumetric flow rates from 20 to 100 Nml/min at a constant S/C 3 and a catalyst weight of 30mg with a particle size of 45µm. The linear velocity of the reactants was varied to assess the external mass transfer limitations.

The external mass transfer limitation was also determined theoretically using following Carberry Number relationship;

$$N_{Ca} = \frac{R_A^{obs}}{k_G a_v C_{Ab}} = \frac{C_{Ab} - C_{As}}{C_{Ab}} < \frac{0.05}{n} \quad (n > 0)$$

9.2.1.3 Internal Heat Transfer Limitations:

To determine the internal heat transfer limitation the Mears criterion of interparticle heat transfer was used;

$$\frac{\Delta H_{rxn} R_A^{obs} \rho_{cat} d_p E}{\lambda_p T^2 R} < 3.0$$

9.2.1.4 External Heat Transfer Limitations:

To determine the external heat transfer limitation the Mears criterion of external heat transfer was used;

$$\frac{\Delta H_{rxn} R_A^{obs} \rho_{cat} d_p E}{h_p T^2 R} < 0.3$$

The detailed calculations are presented in **Appendix**.

9.2.2 S/C ratio and methane partial pressure effect on MSR reaction:

Partial pressure effect of methane and steam was observed from 400-750°C by varying steam to carbon ratio. As no inert gas was used in the reaction system variation of steam to carbon ratio enabled simultaneous change in methane and steam partial pressure. The partial pressure of methane ($P_{CH_4}^*$) and steam ($P_{H_2O}^*$) was varied simultaneously by varying the S/C ratio and keeping the WHSV constant at 0.33NL/g_{cat}-min under isothermal conditions.

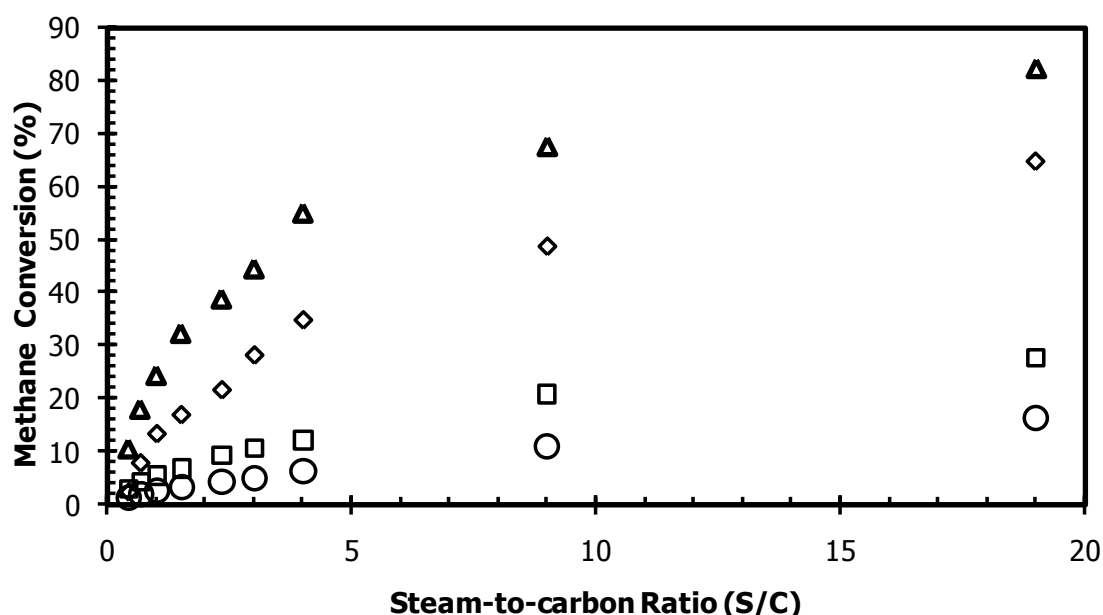


Figure 9.1: Effect of S/C ratio on methane conversion

In terms of methane conversion increase in S/C ratio results in increase in methane conversion. **Figure 9.1** and **Figure 9.2** show the isotherms depicting the effect of S/C ratio and methane partial pressure on methane conversion respectively. Temperature showed a positive effect on methane conversion as

the isotherms show a gradually increment. Till 600°C the isothermal trend remained logarithmic but further increase in temperature changes the trend to third order polynomial.

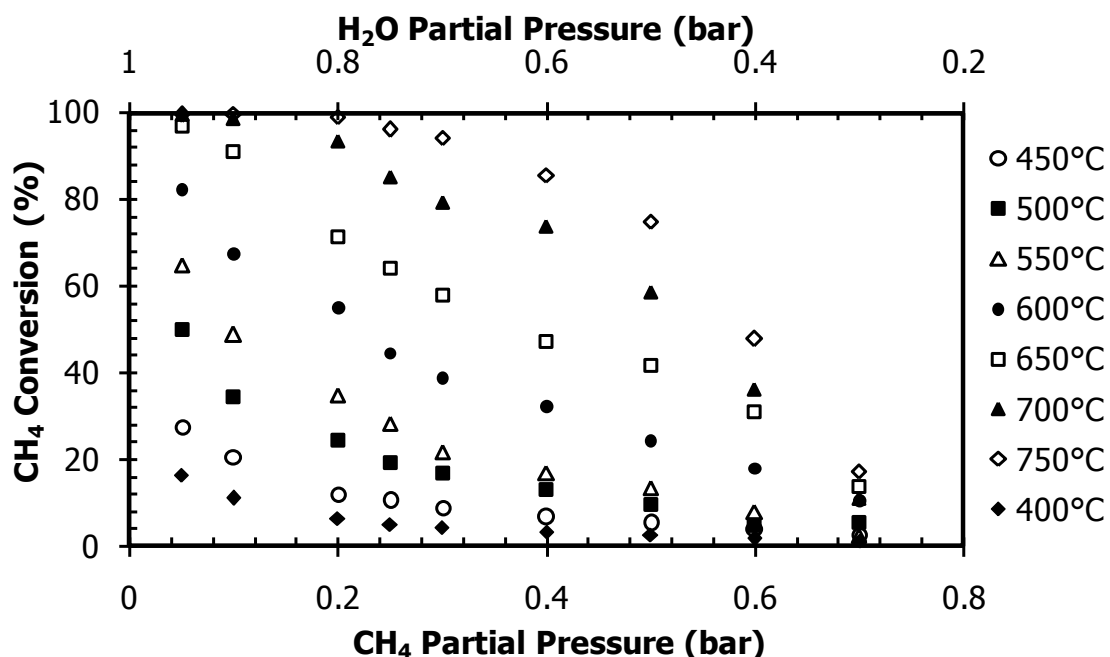


Figure 9.2: Effect of methane and steam partial pressure on methane conversion

A negative effect of the $P_{CH_4}^*$ on methane conversion was observed as the methane conversion decreased gradually with the increase in methane partial pressure. At low temperatures the decrease of methane conversion is slow but with the temperature increment the decrease in methane conversion with partial pressure is significant.

9.2.2.1 Effect of methane Partial Pressure on Product composition and distribution

Figure 9.3 and **Figure 9.4** show the isotherms depicting the effect of methane partial pressure on H₂ dry outlet concentration and CO₂ selectivity.

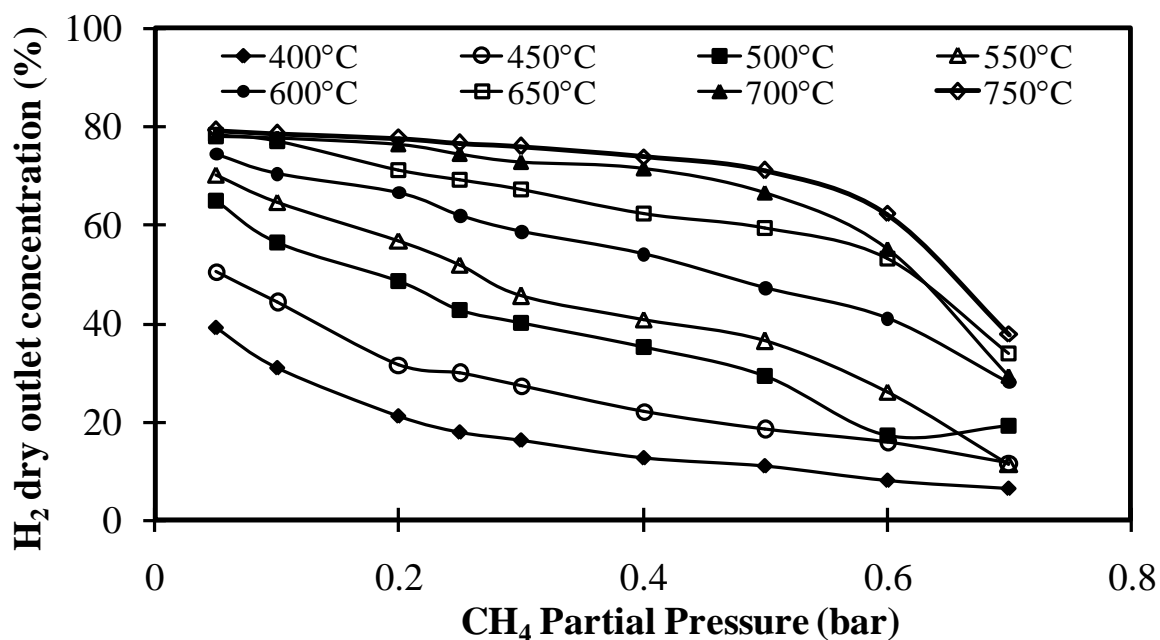


Figure 9.3: Effect of methane partial pressure on H₂ dry outlet concentration

A positive effect of temperature on the H₂ dry outlet concentration was observed, however this effect is less pronounced at temperature above 600°C. A negative effect of methane partial pressure on the H₂ dry outlet concentration was observed, at low methane partial pressure the concentration of H₂ in product stream is high but with the partial pressure increment the H₂ concentration decrease gradually till 550°C. After 550°C the abrupt decrease in H₂ dry outlet concentration with partial pressure increment was observed.

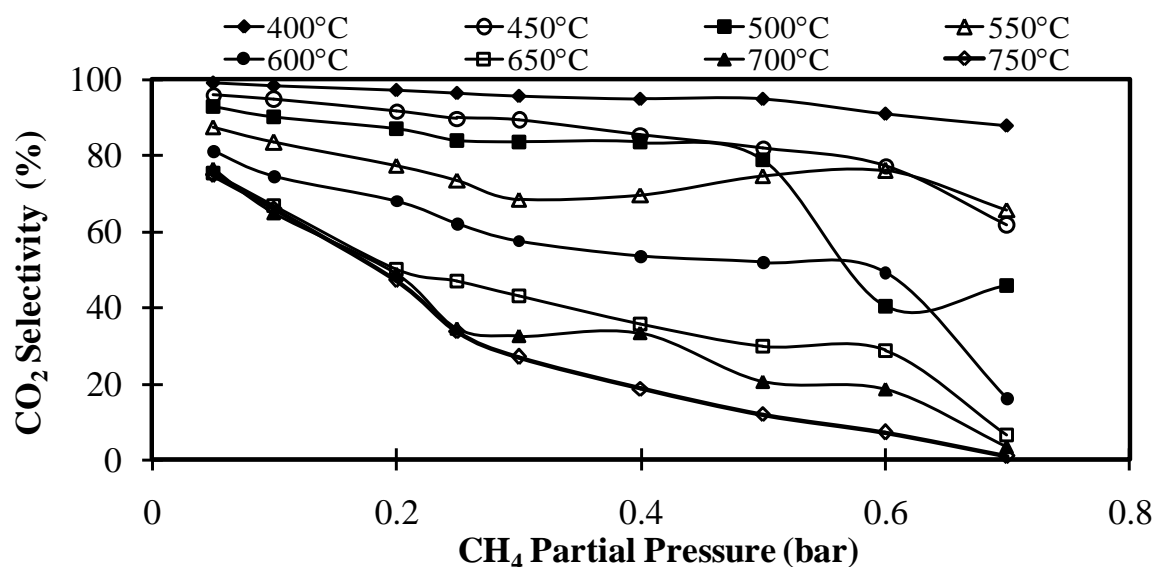


Figure 9.4: Effect of methane partial pressure on CO₂ selectivity

A negative effect of temperature and methane partial pressure on CO₂ selectivity was observed. At low temperature the decrease in CO₂ selectivity with partial pressure increment is slow but at high temperature a sharp decrease in the CO₂ selectivity with partial pressure increment was observed.

9.2.2.2 Effect of methane Partial Pressure on Methane Reaction Rates

The methane reaction rate was calculated by integral method. The methane partial pressure showed a positive effect on methane reaction rate as presented in **Figure 9.5**.

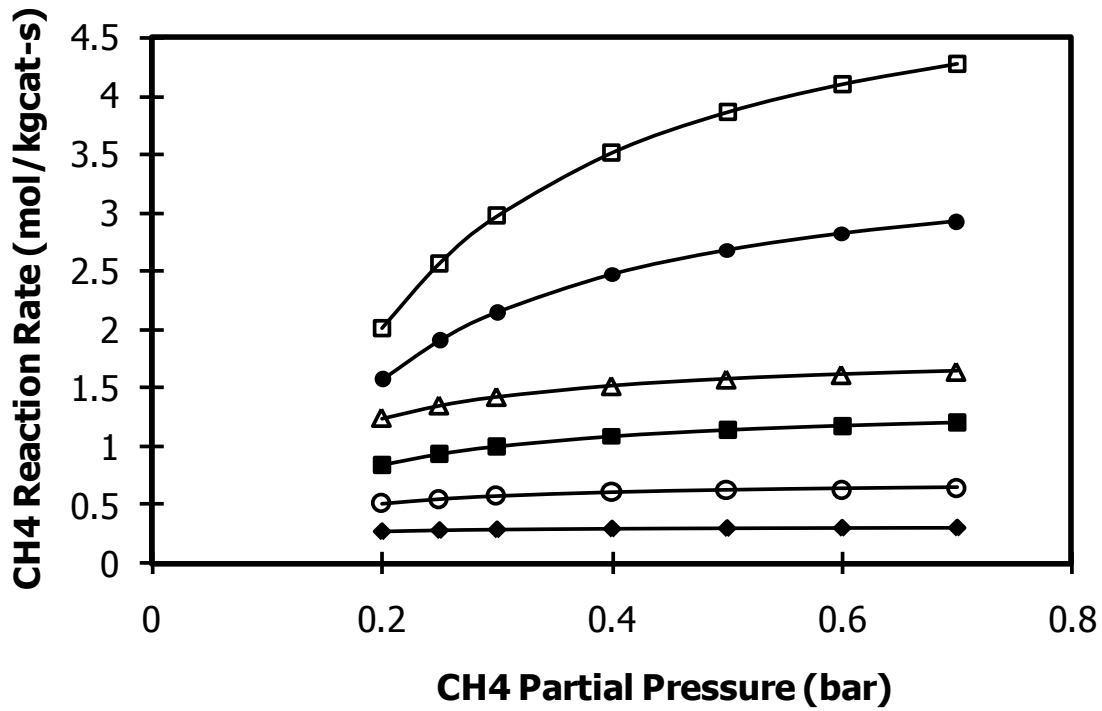


Figure 9.5: Effect of methane partial pressure on methane reaction rate

9.3 Kinetic study:

The steam reforming reaction is performed over a temperature range of 400-600°C and a total pressure of 1atm using a constant S/C ratio of 3. Figure and Figure show the experimental data of the overall methane conversion and methane conversion to CO₂ versus the W/F_{CH₄} (kg_{cat} s mol⁻¹_{CH₄}) respectively. The conversions are calculated according to following equations;

$$x_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}}$$

And

$$x_{CO_2} = \frac{F_{CO_2,out}}{F_{CH_4,in}}$$

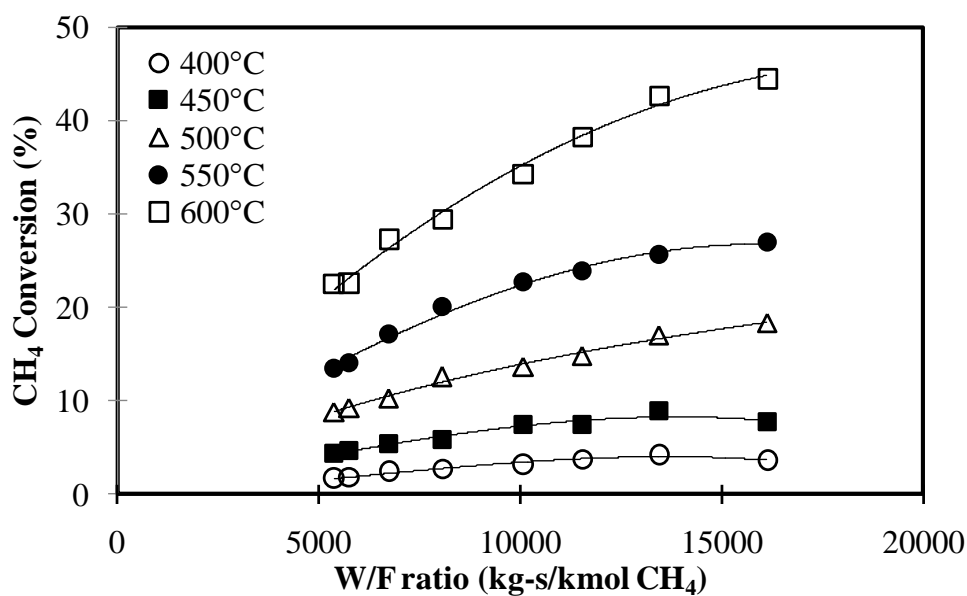


Figure 9.6: Effect of space velocity on methane conversion at S/C 3

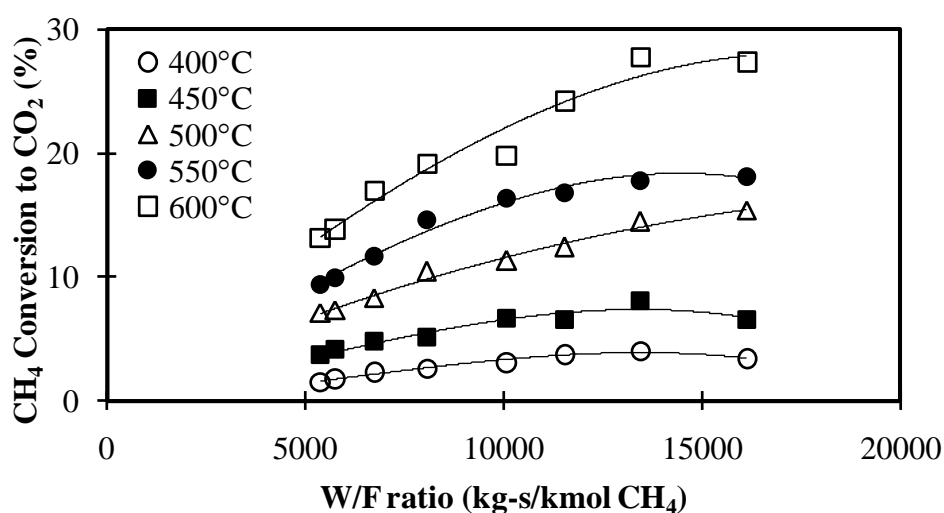


Figure 9.7: Effect of space velocity on methane conversion to CO₂ at S/C 3

9.4 Thermodynamic Analysis:

Possible set of reactions which can occur in MSR along with their equilibrium constant are presented in Table 1^{1,2}.

Table 9.1: Equilibrium constant for reactions involved in MSR

I	Reaction	K_{Pi}	Dimensions
1	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$	$1.167 \times 10^{13} \exp(-26830/T)$	atm ² , bar ²

2	$\text{CO} + 3\text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$	$1.767 \times 10^{-2} \exp(4400/T)$	$\text{atm}^0, \text{bar}^0$
3	$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$	$2.063 \times 10^{11} \exp(-22430/T)$	$\text{atm}^2, \text{bar}^2$
4	$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$	$6.607 \times 10^{14} \exp(-31230/T)$	$\text{atm}^2, \text{bar}^2$
5	$\text{CH}_4 + 3\text{CO}_2 = 4\text{CO} + 2\text{H}_2\text{O}$	$2.115 \times 10^{18} \exp(-40030/T)$	$\text{atm}^2, \text{bar}^2$
6	$\text{CH}_4 = \text{C} + 2\text{H}_2$	$4.107 \times 10^5 \exp(-10614/T)$	atm, bar
7	$2\text{CO} = \text{C} + \text{CO}_2$	$5.818 \times 10^{-10} \exp(20634/T)$	$\text{atm}^{-1}, \text{bar}^{-1}$
8	$\text{CO} + \text{H}_2 = \text{C} + 2\text{H}_2\text{O}$	$3.214 \times 10^{-8} \exp(16318/T)$	$\text{atm}^{-1}, \text{bar}^{-1}$
9	$\text{CO}_2 + 2\text{H}_2 = \text{C} + 2\text{H}_2\text{O}$	$1.775 \times 10^{-6} \exp(12002/T)$	$\text{atm}^{-1}, \text{bar}^{-1}$
10	$\text{CH}_4 + 2\text{CO} = 3\text{C} + 2\text{H}_2\text{O}$	$4.244 \times 10^{-10} \exp(22022/T)$	$\text{atm}^{-1}, \text{bar}^{-1}$
11	$\text{CH}_4 + \text{CO}_2 = 2\text{C} + 2\text{H}_2\text{O}$	$0.730 \exp(1388/T)$	$\text{atm}^0, \text{bar}^0$

From Thermodynamic perspective of reaction system the ratio;

$$V_i = \frac{\left(\prod_j p_j^{v_j}\right)_i}{K_{p_i}}$$

Calculated from experimental results can determine possible direction of a given reaction in following way;

If $V_i < 1$ reaction proceeds right

If $V_i > 1$ reaction proceeds left

From the experimental results from 400-600°C V_i value calculated for reaction 7-10 exceeds 1 therefore no carbon deposition can occur from these reactions. For reaction 5 which corresponds to CO_2 reforming of methane $V_i > 1$ from 400-550°C and $V_i < 1$ from 600-750°C, so this reaction will not occur below 550°C but will be part of reaction system after 600°C. But from analysis of experimental reaction system with increase in methane conversion an increase in CO_2 concentration is observed, thus this reaction is not considered. For reaction 1-4 and 6 V_i value is always less than 1 at all temperatures. As the value for V_6 is less than 1 it means there is a possibility of carbon deposition from decomposition of methane. Isotherms of V_1 as a function of space velocity are presented in fig showing a gradual increase.

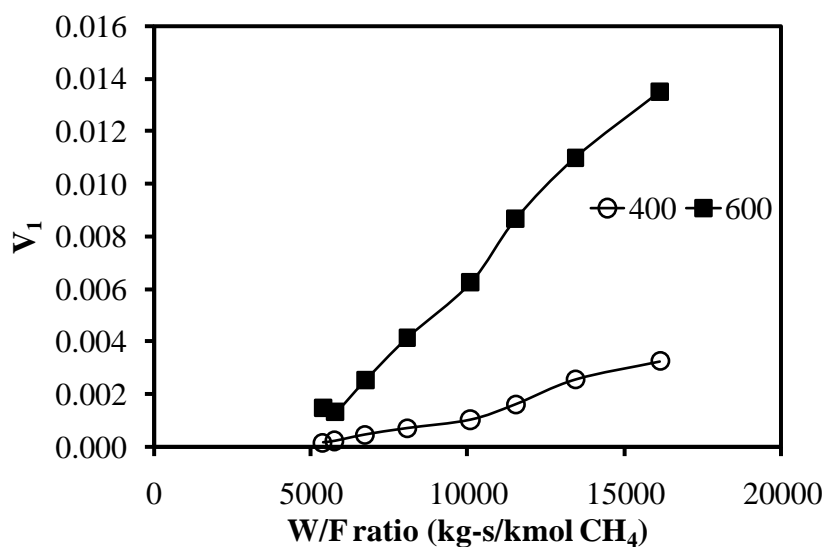


Figure 9.8: Effect of space velocity on extent of MSR reaction

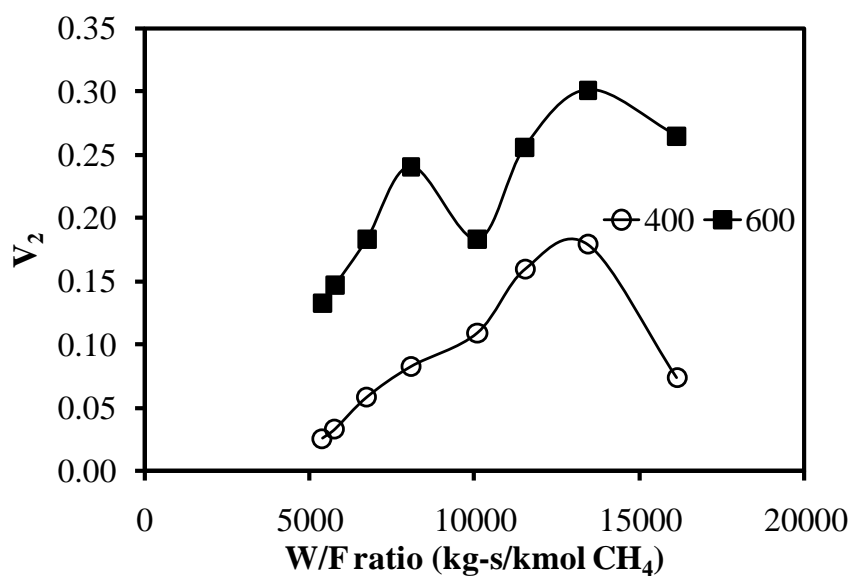


Figure 9.9: Effect of space velocity on extent of water gas shift reaction

It is interesting to note that with increase in temperature from 400-500°C there is a gradual rise in V_1 values indicating a slight decrease in steam reforming reaction potential but after 550°C V_1 values began to lower and at 750°C isotherm lowest values of V_1 are obtained indicating the prevalence of steam reforming reaction.

9.5 Derivation of experimental reaction rates

The obtained experimental methane conversion data is treated in an integral approach. The relationship between overall methane conversion and methane conversion to CO₂ versus inlet space time ($W/F_{CH_4,in}$) at constant pressure and temperature can be analytically described in terms of polynomial functions^{1,3}

$$x_{CH_4} = a_0 + a_1 \frac{W_{cat}}{F_{CH_4,in}} + a_2 \left(\frac{W_{cat}}{F_{CH_4,in}} \right)^2 + a_3 \left(\frac{W_{cat}}{F_{CH_4,in}} \right)^3 \quad (1)$$

$$x_{CO_2} = b_0 + b_1 \frac{W_{cat}}{F_{CH_4,in}} + b_2 \left(\frac{W_{cat}}{F_{CH_4,in}} \right)^2 + b_3 \left(\frac{W_{cat}}{F_{CH_4,in}} \right)^3 \quad (2)$$

Assuming that steam reforming reaction proceeds only in the presence of catalyst; following boundary condition holds

$$\text{At } \frac{W_{cat}}{F_{CH_4,in}} = 0.0, \quad x_{CH_4}, x_{CO_2} = 0.0$$

The parameters in these polynomials are determined by data fitting and are presented in **Table 9.2**.

Table 9.2: Maximum Initial reaction rate Parameters for methane

T (°C)	a ₁ (b ₁)	a ₂ (b ₂)	a ₃ (b ₃)
S/C=3			
400°C	0.333	0.149	-0.016
450°C	1.282	0.057	-0.011
500°C	2.507	-0.116	0.003
550°C	3.301	-0.058	-0.003
600°C	4.914	-0.134	0.000
650°C	8.855	-0.466	0.012
WHSV =0.33 NL/min-g_{cat}			

400°C	0.3202	-0.0008	-0.00001
450°C	0.6987	-0.0046	0.00000
500°C	1.3857	-0.0159	0.00008
550°C	1.8159	-0.0152	0.00003
600°C	3.5867	-0.0608	0.00036
650°C	5.3910	-0.1029	0.00063

Once these polynomial constants are determined, the experimental rate were obtained by differentiating these functions with respect to inlet space time.

$$r_{CH_4} = \frac{dx_{CH_4}}{d\left(\frac{W_{cat}}{F_{CH_4,in}}\right)} = a_1 + 2a_2\left(\frac{W_{cat}}{F_{CH_4,in}}\right) + 3a_3\left(\frac{W_{cat}}{F_{CH_4,in}}\right)^2 \quad (3)$$

$$r_{CO_2} = \frac{dx_{CH_4}}{d\left(\frac{W_{cat}}{F_{CH_4,in}}\right)} = b_1 + 2b_2\left(\frac{W_{cat}}{F_{CH_4,in}}\right) + 3b_3\left(\frac{W_{cat}}{F_{CH_4,in}}\right)^2 \quad (4)$$

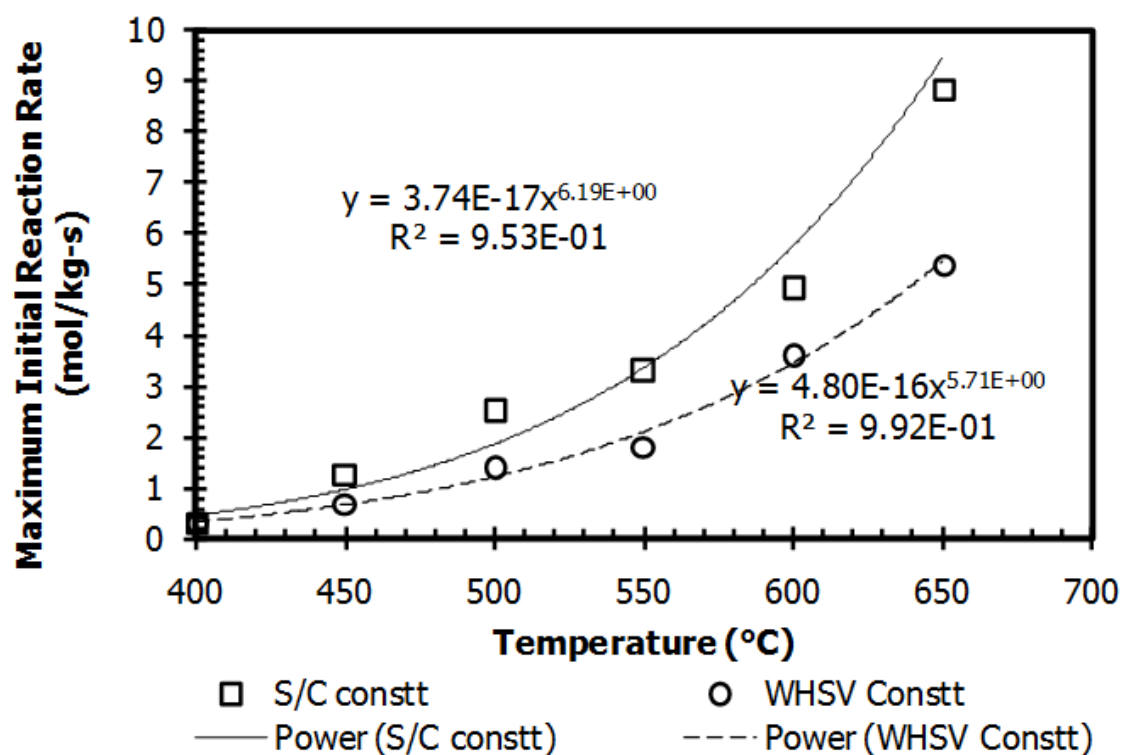


Figure 9.10: Dependence of maximum initial reaction rates on temperature

9.6 Kinetic Model and mechanism of methane steam reforming:

An attempt was made to fit the experimental data with the models proposed in literature for Ni, Rh and Ru catalysts. The list of models is presented in Table

Model	
Xu & Froment ² Ni catalyst	$Rate = \frac{kP_{CH_4}P_{H_2}^{2.5}}{P_{H_2} \left(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} + K_{CH_4}P_{CH_4} \right)}$

Model	
Halabi ³ Rh catalyst	$Rate = \frac{\frac{k}{P_{H_2}^{2.5}} \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eq}} \right)}{\left(1 + K_{CH_4} \frac{P_{CH_4}}{P_{H_2}} + K_{H_2} P_{H_2} + K_{CO} P_{CO} \right) \left(1 + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} + K_{H_2} P_{H_2} \right)}$
Hou ¹ Ni catalyst	$Rate = \frac{\frac{k}{P_{H_2}^{1.75}} \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eq}} \right)}{1 + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} + K_H P_H^{0.5} + K_{CO} P_{CO}}$
Jakobsen ⁴ Rh catalyst	$Rate = \frac{A \exp\left(\frac{-E}{RT}\right) P_{CH_4} (1 - b)}{\left(1 + A_{CO} \exp\left(\frac{-\Delta H_{CO}}{RT}\right) P_{CO} + A_H \exp\left(\frac{-\Delta H_H}{RT}\right) P_{H_2}^{0.5} \right)^2}$
Wei & Iglesia ⁵ Rh catalyst	$Rate = k P_{CH_4}$
Berman ⁶ Ru catalyst	$Rate = \frac{k P_{CH_4}}{b_{CH_4} P_{CH_4} + b_{H_2O} P_{H_2O}^{0.5}}$
Power Law ⁷ Ni catalyst	$Rate = k P_{CH_4}^n P_{H_2O}^m$

The parameter estimation and model discrimination was based on minimizing sum of squares (SSQ) of the outlet methane conversion by using following equation

$$SSQ = \sum_{i=1}^n (X_{calculated} - X_{measured})^2 \quad (I)$$

The accuracy of parameter estimate is determined by its t-value and 95% confidence interval.

The discrimination between the models is conducted based on the physical consideration of parameter estimate. If the model results in negative values

which should be positive the model was rejected. Additionally the goodness of fit was estimated by the parity diagram.

Based on the above criteria, only Berman's models fit the experimental data as shown by the parity diagram in **Figure 9.11**

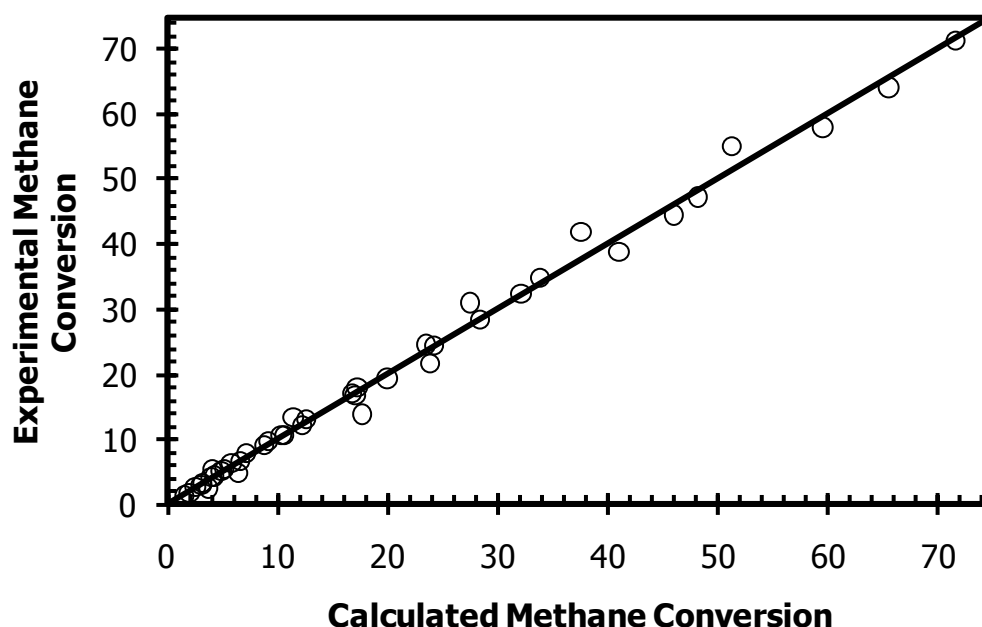


Figure 9.11: Parity diagram for Berman's model fit

The activation energy value calculated for Rh/CeO₂ from our experimental data is 38.6 kJ/mol. This value is very low compared to other activation energies on supported Rh catalyst. Wei & Iglesia⁵ found steam reforming activation energy of 109 kJ/mol on Rh/Al₂O₃ surface while Halabi et al.³ reported an activation energy of 83.8 kJ/mol on Rh/Ce_{0.6}Zr_{0.4}O₂ catalyst. Jakobsen et al.⁴ reported an activation energy of 89 kJ/mol on Rh/ZrO₂ catalyst and Zeppieri et al.⁸ evaluated an activation energy of 69.1 kJ/mol on Rh-perovskite catalyst.

For pure Rh metal, a methane activation energy of 29 kJ/mol and 46.4 kJ/mol on Rh films⁸ for dissociative adsorption of CH₄ has been reported. Liu et al.⁹ by using density functional theory (DFT) calculated the activation energy of CH₄ dissociation reaction on Rh and reported C-H activation energy of 67, 32 and 20 kJ/mol on flat, stepped and kinked Rh surface respectively. The theoretical estimates are in

good agreement with the activation energy of 38.6 kJ/mol found in this work for Rh/CeO₂ catalyst.

9.7 References:

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- (2) Xu, J.; Froment, G. F. Methane Steam Reforming, Methanation and Water-Gas Shift: I. Intrinsic Kinetics. *AIChE Journal* **1989**, *35*, 88–96.
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- (7) Ko, K.-D.; Lee, J. K.; Park, D.; Shin, S. H. Kinetics of Steam Reforming over a Ni/alumina Catalyst. *Korean J. Chem. Eng.* **1995**, *12*, 478–480.
- (8) Zeppieri, M.; Villa, P. L.; Verdone, N.; Scarsella, M.; De Filippis, P. Kinetic of Methane steam reforming Reaction over Nickel- and Rhodium-Based Catalysts. *Applied Catalysis A: General* **2010**, *387*, 147–154.
- (9) Liu, Z.-P.; Hu, P. General Rules for Predicting Where a Catalytic Reaction Should Occur on Metal Surfaces: A Density Functional Theory Study of C–H and C–O Bond Breaking/Making on Flat, Stepped, and Kinked Metal Surfaces. *J. Am. Chem. Soc.* **2003**, *125*, 1958–1967.

Chapter 10 Conclusion

The Rh catalysts on the MgO, the niobic acid and the niobia supports were tested towards MSR reaction at S/C 4 with the WSV of $0.33 \text{ NL min}^{-1} \text{ g}_{\text{cat}}^{-1}$ and low temperature range of 400-750°C. Among the five catalysts prepared, only MgO supported Rh achieved full methane conversion, while the other four catalysts although active towards MSR could only reach a maximum of 88% methane conversion. However further investigations regarding endurance and S/C variation of these catalysts can ensure the stability of the catalysts.

The Ru catalysts on MgO, niobic acid and niobia supports were tested towards the MSR reaction between 400 and 750 °C, with steam-to-carbon equal to 4 and weight space velocity equal to $0.33 \text{ NL min}^{-1} \text{ g}_{\text{cat}}^{-1}$. Among ten different catalysts prepared, at 700-750°C only six of them achieved full CH₄ conversion, while the other catalysts reached only a maximum of 80% CH₄ conversion. The best catalysts were slightly more active at 700°C than at 750°C. The morphological and surface characteristics suggest that catalysts with amorphous structure and Ru/support atomic surface ratio less than 1 were more selective towards CO₂ compared to catalysts with crystalline structure.

Finally for **Part I** different noble metals (Rh, Ru and Pt) deposited on two different oxide carriers (CeO₂ and Al₂O₃) were synthesized, characterized and tested towards MSR and methane oxidative steam reforming reactions. All of the catalysts showed complete methane conversion, for both reactions, at different minimum temperatures. A comparative analysis pointed out the 1.5% Rh/CeO₂ as the best catalyst for methane SR reaction as it gave very good catalytic activity at the lower reaction temperature: complete methane conversion at 635 °C, with carbon dioxide selectivity of 87.5% and outlet hydrogen concentration of 74.4% (volume dry reformat). Also the 1.5% Ru/Al₂O₃ showed good performance for OSR reaction, but at higher temperature, and with slightly lower CO₂ selectivity and hydrogen outlet concentration.

The 1.5% Rh/CeO₂ catalyst for methane SR reaction provided desirable results at relatively low temperature for generating a hydrogen-rich gas with low content of carbon monoxide. This would be very appropriate in case of fuel processors where it is necessary to minimize as much as possible the residual carbon monoxide concentration, for feeding PEM-FCs, as the following CO clean-up process can be reduced in size and volume.

From **Part I** the best catalysts found to be active for MSR were tested towards the stability under cyclic conditions and continuous operation in **Part II**.

The SCS prepared Pt/CeO₂ performance and ageing was analyzed for MSR reaction in low temperature range 400-750°C. The obtained result showed that the catalyst is more active at low WHSV (0.33 l min⁻¹ g_{cat}⁻¹) and performs better at low S/C ratio (2.8) as it produces 76% H₂ with 61% CO₂ selectivity in dry outlet gas stream with 99% methane conversion at 700°C. Stability test carried out at 700°C for 150h ensures high catalytic activity and stability under cyclic conditions, and is mainly attributed to strong metal support interaction generated through formation of solid solution during solution combustion synthesis. Also the structure of the catalyst is responsible for resistance to sintering and coking as shown by the characterization of used catalyst.

The Rh/CeO₂ catalyst performance and ageing was analyzed for MSR reaction in low temperature range 400-750°C. Stability test carried out at 750°C for 100h ensures high catalytic activity and stability and is mainly attributed to strong metal support interaction generated within the catalyst. Also the structure of the catalyst is responsible for resistance to sintering and coking as shown by the characterization of used catalyst.

From **Part II** the best catalysts found to be stable under cyclic conditions and continuous operation was tested to determine the intrinsic kinetics for MSR in **Part III**. The intrinsic kinetics of Rh/CeO₂ catalyst was evaluated between 400°C-650°C in integral mode reactor at 1 atm pressure. The data obtained from Rh/CeO₂ catalyst followed Berman Model and resulted in activation energy of 38.6 kJ/mol.

List of Publications:

Chapter 6 was presented at 3rd North American Symposium on Chemical Reaction Engineering (NASCRE-3), Houston (TX), USA, 17-20/03/2013 and published as: "A Comparative Study on Steam and Oxidative Steam Reforming of Methane with Noble Metal Catalysts" was published in ACS journal INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 52 n. 44, pp. 15428-15436. - ISSN 0888-5885

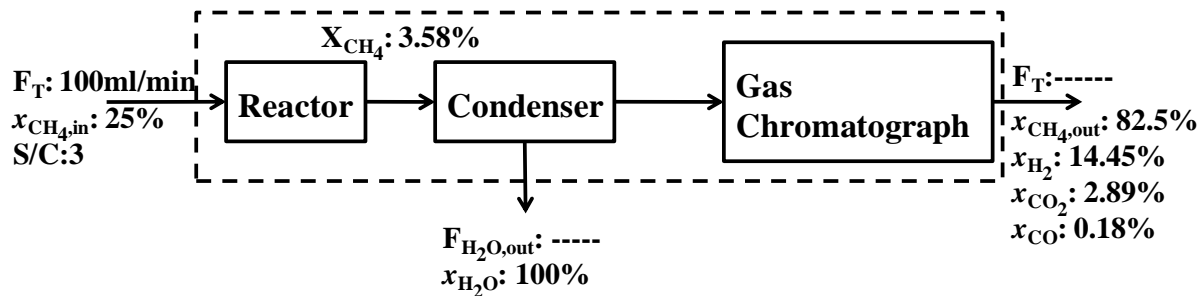
Chapter 5 has been presented at International Symposium on Air & Water Pollution Abatement Catalysis - AWPAC2014, Krakow (Poland), 1-5/09/2014. p. 59 and submitted as "MgO and Nb₂O₅ oxides used as supports for Ru-based catalysts for the methane steam reforming reaction" to the peer reviewed journal Catalysis Today with the manuscript number CATTOD-S-14-00969-1

The manuscript for **Chapter 3**, **Chapter 7**, **Chapter 8** and **Chapter 9** are in preparation and will be submitted to peer reviewed journals in the next future

Appendices

Mass Balance:

To convert the dry outlet concentration to wet concentration the mass balance was applied to evaluate the water concentration and partial pressures of the components based on wet concentration.



Basis: 1min=60s

Total Flow = $F_T = 100\text{ml}$

Methane flow = $F_{CH_4} = x_{CH_4} \times F_T = 0.25 \times 100 = 25\text{ml}$

Methane flow = $F_{CH_4,in} = x_{CH_4} \times F_T = 0.25 \times 100 = 25\text{ ml}$

$$\frac{25\text{ml}}{\text{min}} \times \frac{\text{mmol}}{22.4\text{ ml}} \times \frac{1\text{ mol}}{1000\text{mmol}} \times \frac{1\text{kmol}}{1000\text{mol}} \times \frac{1\text{min}}{60\text{s}} = 1.86 \times 10^{-8} \frac{\text{kmol}}{\text{s}}$$

As $S/C=3$ so,

Steam flow = $F_{H_2O,in} = 3 \times F_{CH_4} = 3 \times 1.86 \times 10^{-8} = 5.58 \times 10^{-8} \text{ kmol}$

$F_{T,in} = F_{CH_4,in} + F_{H_2O,in} = 1.86 \times 10^{-8} + 5.58 \times 10^{-8} = 7.44 \times 10^{-8} \text{ kmol}$

Based on the carbon balance the total outlet flow is;

$$F_{T,out} = \frac{F_{CH_4,in}}{x_{CH_4,out} + x_{CO_2} + x_{CO}}$$

$$F_{T,out} = \frac{1.86 \times 10^{-8} \times 100}{(82.5 + 2.89 + 0.18)} = 2.17 \times 10^{-8} \text{ kmol}$$

So corresponding outlet moles are;

$$F_{CH_4,out} = \frac{x_{CH_4,out} \times F_{T,out}}{100} = \frac{82.5 \times 2.17 \times 10^{-8}}{100} = 1.79 \times 10^{-8} \text{ kmol}$$

$$F_{CO_2,out} = \frac{x_{CO_2,out} \times F_{T,out}}{100} = \frac{2.89 \times 2.17 \times 10^{-8}}{100} = 6.27 \times 10^{-10} \text{ kmol}$$

$$F_{H_2,out} = \frac{x_{H_2,out} \times F_{T,out}}{100} = \frac{14.45 \times 2.17 \times 10^{-8}}{100} = 3.13 \times 10^{-9} \text{ kmol}$$

$$F_{CO,out} = \frac{x_{CO,out} \times F_{T,out}}{100} = \frac{0.18 \times 2.17 \times 10^{-8}}{100} = 3.91 \times 10^{-11} \text{ kmol}$$

Based on overall mass balance;

$$F_{H_2O,out} = F_{T,in} - F_{T,out} = 7.44 \times 10^{-8} - 2.17 \times 10^{-8} = \mathbf{5.27 \times 10^{-8} kmol}$$

So overall outlet flow is;

$$F'_{T,out} = F_{T,in} = F_{T,out} + F_{H_2O,out} = 7.44 \times 10^{-8} + 5.27 \times 10^{-8} = 2.17 \times 10^{-8} \text{ kmol}$$

To convert to partial pressure following equation was used,

$$P_{CH_4}^* = \frac{F_{CH_4,out}}{F'_{T,out}} \times P_T = \frac{1.79 \times 10^{-8} \text{ kmol} \times 1 \text{ atm}}{2.17 \times 10^{-8} \text{ kmol}} = \mathbf{0.239 \text{ atm}}$$

$$P_{CO_2}^* = \frac{F_{CO_2,out}}{F'_{T,out}} \times P_T = \frac{0.019 \text{ mol} \times 1 \text{ atm}}{2.24 \text{ mol}} = \mathbf{0.0085 \text{ atm}}$$

$$P_{H_2}^* = \frac{F_{H_2,out}}{F'_{T,out}} \times P_T = \frac{0.094 \text{ mol} \times 1 \text{ atm}}{2.24 \text{ mol}} = \mathbf{0.042 \text{ atm}}$$

$$P_{CO}^* = \frac{F_{CO,out}}{F'_{T,out}} \times P_T = \frac{0.0012 \text{ mol} \times 1 \text{ atm}}{2.24 \text{ mol}} = \mathbf{0.00054 \text{ atm}}$$

$$P_{H_2O,out}^* = \frac{F_{H_2O,out}}{F'_{T,out}} \times P_T = \frac{1.59 \text{ mol} \times 1 \text{ atm}}{2.24 \text{ mol}} = \mathbf{0.71 \text{ atm}}$$

Average Molecular weight of the gas mixture;

$$M_{avg} = \sum_{i=1}^5 y_i M_i$$

$$M_{avg} = y_{CH_4} M_{CH_4} + y_{CO_2} M_{CO_2} + y_{H_2} M_{H_2} + y_{CO} M_{CO} + y_{H_2O} M_{H_2O}$$

Where;

$$y_{CH_4} = \frac{P_{CH_4}^*}{P_T}, \quad y_{CO_2} = \frac{P_{CO_2}^*}{P_T}, \quad y_{H_2} = \frac{P_{H_2}^*}{P_T}, \quad y_{CO} = \frac{P_{CO}^*}{P_T}, \quad y_{H_2O} = \frac{P_{H_2O,out}^*}{P_T}$$

So,

$$M_{avg} = (0.239 \times 16) + (0.0085 \times 44) + (0.042 \times 2) + (0.00054 \times 28) + (0.71 \times 18)$$

$$M_{avg} = \mathbf{17.083 kg/kmol}$$

So, at 400°C the fluid density is;

$$\rho_f = \frac{M_{avg}}{22.4} \frac{273}{T}$$

$$\rho_f = \frac{17.083}{22.4} \times \frac{273}{(400 + 273)}$$

$$\rho_f = \mathbf{0.3093 kg/m^3}$$

To calculate the fluid mixture viscosity Wilke equation (1950) was used

$$\mu_m = \frac{\sum \mu_i y_i M_i^{1/2}}{\sum y_i M_i^{1/2}}$$

At 400°C,

$$\mu_{CH_4} = 2.119 \times 10^{-5} kgm^{-1}s^{-1}$$

$$\mu_{CO_2} = 3.061 \times 10^{-5} kgm^{-1}s^{-1}$$

$$\mu_{H_2} = 1.57 \times 10^{-5} kgm^{-1}s^{-1}$$

$$\mu_{CO} = 3.111 \times 10^{-5} \text{kgm}^{-1}\text{s}^{-1}$$

$$\mu_{H_2O} = 2.446 \times 10^{-5} \text{kgm}^{-1}\text{s}^{-1}$$

Component	y_i	M_i	μ_i	$y_i M_i^{1/2}$	$\mu_i y_i M_i^{1/2}$
CH ₄	0.239	16	2.119×10^{-5}	0.944	2×10^{-5}
CO ₂	0.0082	44	3.061×10^{-5}	0.054	1.65×10^{-6}
H ₂	0.041	2	1.57×10^{-5}	0.058	9.106×10^{-7}
CO	0.0005	28	3.111×10^{-5}	0.0026	8.08×10^{-8}
H ₂ O	0.71	18	2.446×10^{-5}	3.025	7.4×10^{-5}
			Σ	4.0836	9.66×10^{-5}

So,

Viscosity of gas mixture is;

$$\mu_{mix} = \frac{\sum \mu_i y_i M_i^{1/2}}{\sum y_i M_i^{1/2}} = \frac{9.66 \times 10^{-5}}{4.0836} = 2.366 \times 10^{-5} \text{kgm}^{-1}\text{s}^{-1}$$

Mass Transfer Limitation:

To calculate diffusion, Fuller equation (1966) was used;

$$D_{ij} = \frac{10^{-3} T^{1.75} \left(\frac{1}{M_i} - \frac{1}{M_j} \right)^{1/2}}{P_T \left(\sum v_i^{1/3} + \sum v_j^{1/3} \right)^2}$$

Where;

$v_{i,j}$ = diffusion volumes of gas components

And

$$v_{CH_4} = 24.42, \quad v_{H_2} = 7.07, \quad v_{CO_2} = 18.9, \quad v_{CO_2} = 26.9, \quad v_{H_2O} = 12.7$$

As CH₄ is the limiting reactant, the binary diffusivity D_{ij} was calculated of all the components with respect to CH₄, so,

$$D_{CH_4-H_2} = \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{M_{CH_4}} + \frac{1}{M_{H_2}} \right)^{1/2}}{P_T \left(\nu_{CH_4}^{1/3} + \nu_{H_2}^{1/3} \right)^2}$$

$$= \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{16} + \frac{1}{2} \right)^{1/2}}{1 \times (24.42^{1/3} + 7.07^{1/3})^2} = 2.87 \text{ cm}^2 \text{ s}^{-1}$$

$$D_{CH_4-CO_2} = \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{M_{CH_4}} + \frac{1}{M_{CO_2}} \right)^{1/2}}{P_T \left(\nu_{CH_4}^{1/3} + \nu_{CO_2}^{1/3} \right)^2}$$

$$= \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{16} + \frac{1}{44} \right)^{1/2}}{1 \times (24.42^{1/3} + 26.9^{1/3})^2} = 0.743 \text{ cm}^2 \text{ s}^{-1}$$

$$D_{CH_4-H_2O} = \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{M_{CH_4}} + \frac{1}{M_{H_2O}} \right)^{1/2}}{P_T \left(\nu_{CH_4}^{1/3} + \nu_{H_2O}^{1/3} \right)^2}$$

$$= \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{16} + \frac{1}{18} \right)^{1/2}}{1 \times (24.42^{1/3} + 12.7^{1/3})^2} = 1.11 \text{ cm}^2 \text{ s}^{-1}$$

$$D_{CH_4-CO} = \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{M_{CH_4}} + \frac{1}{M_{CO}} \right)^{1/2}}{P_T \left(\nu_{CH_4}^{1/3} + \nu_{CO}^{1/3} \right)^2}$$

$$= \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{16} + \frac{1}{28} \right)^{1/2}}{1 \times (24.42^{1/3} + 18.9^{1/3})^2} = 0.903 \text{ cm}^2 \text{ s}^{-1}$$

$$D_{CH_4-CH_4} = \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{M_{CH_4}} + \frac{1}{M_{CH_4}} \right)^{1/2}}{P_T \left(\nu_{CH_4}^{1/3} + \nu_{CH_4}^{1/3} \right)^2}$$

$$= \frac{10^{-3}(400 + 273)^{1.75} \left(\frac{1}{16} + \frac{1}{16} \right)^{1/2}}{1 \times (24.42^{1/3} + 24.42^{1/3})^2} = 0.925 \text{ cm}^2 \text{ s}^{-1}$$

Based on the binary diffusion calculation the mixture diffusion is given by Fairbans & Wilke equation (1950) as;

$$D_{CH_4-mix} = \frac{1 - y_{CH_4}}{\sum_{j \neq 1} \frac{y_j}{D_{ij}}}$$

$$\begin{aligned} D_{CH_4-mix} &= \frac{1 - y_{CH_4}}{\frac{y_{CO_2}}{D_{CH_4-CO_2}} + \frac{y_{CO}}{D_{CH_4-CO}} + \frac{y_{H_2}}{D_{CH_4-H_2}} + \frac{y_{H_2O}}{D_{CH_4-H_2O}}} \\ &= \frac{1 - 0.239}{\frac{0.0082}{0.743} + \frac{0.0005}{0.903} + \frac{0.041}{2.87} + \frac{0.71}{1.11}} = \frac{1.144 \text{ cm}^2 \text{ s}^{-1}}{(100)^2 \text{ cm}^2} \\ &= \mathbf{1.144 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}} \end{aligned}$$

The effective diffusivity is calculated from the relation in Fogler as;

$$D_{A,eff} = \frac{D_{CH_4-mix} \phi_p \sigma_c}{\tau}$$

Where;

$$\phi_p = \text{Pellet porosity} = 0.40$$

$$\sigma_c = 0.8$$

$$\tau = \text{Tortosity} = 3.0$$

So effective diffusivity is;

$$D_{CH_4,eff} = \frac{1.144 \times 10^{-4} \times 0.4 \times 0.8}{3} = \mathbf{1.22 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}}$$

The Schmidt number calculated on the basis of effective diffusivity is;

$$N_{Sc} = \frac{\mu_{mix}}{\rho_f D_{CH_4,eff}} = \frac{2.366 \times 10^{-5}}{0.309 \times 1.22 \times 10^{-5}} = \mathbf{6.24}$$

And the Reynolds number is;

$$N_{Re} = \frac{d_p \rho_f v_s}{\mu_{mix}}$$

Where;

$$d_p = \text{Particle diameter} = 0.15 \text{ mm} = \mathbf{0.15 \times 10^{-3} \text{ m}}$$

$$v_s = \text{superfacial velocity} = \frac{F_T}{A}$$

$$F_T = \frac{100\text{ml}}{\text{min}} \times \frac{1\text{min}}{60\text{s}} \times \frac{1\text{L}}{1000\text{ml}} \times \frac{1\text{m}^3}{1000\text{L}} = 1.66 \times 10^{-6} \text{m}^3 \text{s}^{-1}$$

$$A = \frac{\pi d^2}{4} = \frac{\pi}{4} \times \left(4\text{mm} \times \frac{1\text{m}}{1000\text{mm}}\right)^2 = 1.25 \times 10^{-5} \text{m}^2$$

So,

$$v_s = \frac{F_T}{A} = \frac{1.66 \times 10^{-6}}{1.25 \times 10^{-5}} = \mathbf{0.1328 \text{ms}^{-1}}$$

So, the Reynolds number is,

$$N_{Re} = \frac{0.15 \times 10^{-3} \times 0.309 \times 0.1328}{2.366 \times 10^{-5}} = \mathbf{0.26}$$

Sherwood number is calculated using the Froessling relation;

$$N_{Sh} = 2 + 0.552 N_{Re}^{1/2} N_{Sc}^{1/3} = 2 + 0.552 (0.26)^{1/2} (6.24)^{1/3} = \mathbf{2.52}$$

Putting the values in following equation;

$$N_{Sh} = \frac{k_G d_p}{D_{eff}}$$

$$2.52 = \frac{k_G \times 0.15 \times 10^{-3}}{1.22 \times 10^{-5}} \Rightarrow k_G = \frac{2.52 \times 1.22 \times 10^{-5}}{0.15 \times 10^{-3}} = \mathbf{0.205 \text{ m/s}}$$

External Mass Transfer Limitation:

Carberry Number;

$$N_{Ca} = \frac{R_A^{obs}}{k_G a_v C_{Ab}} = \frac{C_{Ab} - C_{As}}{C_{Ab}} < \frac{0.05}{n} \quad (n > 0)$$

$$R_A^{obs} = 3.95 \times 10^{-5} \text{mol s}^{-1} \text{kg}^{-1} = 3.95 \times 10^{-8} \text{kmol s}^{-1} \text{kg}^{-1}$$

$$a_v = 2.05 \text{m}^2 \text{g}_{cat}^{-1} = 2.05 \times 10^3 \text{m}^2 \text{kg}_{cat}^{-1}$$

$$C_{Ab} = \frac{F_{\text{CH}_4}}{F_T} = \frac{1.86 \times 10^{-8} \text{kmol}}{\text{s}} \times \frac{\text{s}}{1.66 \times 10^{-6} \text{m}^3} = 0.0112 \frac{\text{kmol}}{\text{m}^3}$$

So,

$$N_{Ca} = \frac{R_A^{obs}}{k_G a_v C_{Ab}} = \frac{3.95 \times 10^{-8} kmol}{kg_{cat} s} \times \frac{kg_{cat}}{2.05 \times 10^3 m^2} \times \frac{m^3}{0.0112 kmol} \times \frac{s}{0.205 m}$$

$$= 8.39 \times 10^{-10}$$

$$N_{Ca} = \frac{C_{Ab} - C_{As}}{C_{Ab}} \Rightarrow 8.39 \times 10^{-10} = \frac{0.0112 - C_{As}}{0.0112}$$

$$C_{As} = 0.0112 - (8.39 \times 10^{-10} \times 0.0112) = \frac{0.01119 kmol}{m^3}$$

For external mass transfer limitations following criterion must be fulfilled;

$$N_{Ca} < \frac{0.05}{n} \quad (n > 0)$$

Where n=reaction order

From 400°C to 650°C the methane reaction order n = 1

So,

$$N_{Ca} < \frac{0.05}{n} \quad (n > 0)$$

$$8.39 \times 10^{-10} < \frac{0.05}{1} \quad (n > 0)$$

$$8.39 \times 10^{-10} \ll 0.05$$

So; external mass transfer limitations are OK.

Internal Diffusion Limitation:

Weisz-Prater Criterion:

$$C_{WP} = \frac{R_A^{obs} \rho_c R^2}{D_{A,eff} C_{As}}$$

$$C_{WP} = \frac{3.95 \times 10^{-8} \text{ kmol}}{\text{kg}_{cat} \text{ s}} \times \frac{6957 \text{ kg}}{\text{m}^3} \times \left(\frac{0.15 \times 10^{-3} \text{ m}}{2} \right)^2 \times \frac{\text{s}}{1.22 \times 10^{-5} \text{ m}^2} \\ \times \frac{\text{m}^3}{0.01119 \text{ kmol}}$$

$$C_{WP} = 5.66 \times 10^{-6} \ll 1$$

so no internal diffusion is present.

Heat Transfer Limitation:

$$C_{p,mix} = \frac{\sum_{i=1}^n y_i C_{p,i}}{M_{avg}}$$

At 400°C,

$$C_{p,CH_4} = 3836 \text{ J kg}^{-1} \text{ K}^{-1}, \quad C_{p,CO_2} = 1156 \text{ J kg}^{-1} \text{ K}^{-1},$$

$$C_{p,CO} = 1135 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$C_{p,H_2} = 14653 \text{ J kg}^{-1} \text{ K}^{-1}, \quad C_{p,H_2O} = 2137 \text{ J kg}^{-1} \text{ K}^{-1},$$

So,

$$\sum_{i=1}^n y_i C_{p,i} = y_{CH_4} C_{p,CH_4} + y_{CO_2} C_{p,CO_2} + y_{H_2} C_{p,H_2} + y_{CO} C_{p,CO} + y_{H_2O} C_{p,H_2O}$$

$$\sum_{i=1}^n y_i C_{p,i} = (0.239 \times 3836) + (0.0085 \times 1156) + (0.042 \times 14653)$$

$$+ (0.00054 \times 1135) + (0.71 \times 2137) = 3060 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$C_{p,mix} = \frac{3060 \text{ J kg}^{-1} \text{ K}^{-1}}{17.083 \text{ kg kmol}^{-1}}$$

At 400°C,

$$\lambda_{CH_4} = 0.11933 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\lambda_{CO_2} = 0.05293 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\lambda_{H_2} = 0.3509 \text{ Wm}^{-1}\text{K}^{-1}$$

$$\lambda_{CO} = 0.05412 \text{ Wm}^{-1}\text{K}^{-1}$$

$$\lambda_{H_2O} = 0.06677 \text{ Wm}^{-1}\text{K}^{-1}$$

Component	y_i	M_i	λ_i	$y_i M_i^{1/3}$	$\lambda_i y_i M_i^{1/3}$
CH ₄	0.239	16	0.11933	0.602	0.072
CO ₂	0.0082	44	0.05293	0.029	0.002
H ₂	0.041	2	0.3509	0.052	0.018
CO	0.0005	28	0.05412	0.002	0.000
H ₂ O	0.71	18	0.06677	1.861	0.124
			Σ	2.545	0.216

So,

Thermal conductivity of gas mixture is;

$$\lambda_{mix} = \frac{\sum \lambda_i y_i M_i^{1/3}}{\sum y_i M_i^{1/3}} = \frac{0.216}{2.545} = \mathbf{0.085 \text{ Wm}^{-1}\text{K}^{-1}}$$

So, Prandtl Number is;

$$N_{Pr} = \frac{\mu_{mix} C_{p,mix}}{\lambda_{mix}} = \frac{2.366 \times 10^{-5} \text{ kg}}{\text{m s}} \times \frac{3060 \text{ J}}{\text{kgK}} \times \frac{\text{m K}}{0.085 \text{ W}} = 0.852$$

$$N_{Nu} = 2 + 1.1 N_{Re}^{0.6} N_{Pr}^{1/3}$$

$$N_{Nu} = 2 + 1.1(0.26)^{0.6}(0.852)^{1/3} = \mathbf{2.464}$$

$$N_{Nu} = \frac{h_p d_p}{\lambda_{mix}} \Rightarrow 2.464 = \frac{h_p \times 0.15 \times 10^{-3}}{0.085} \Rightarrow h_p = \frac{2.464 \times 0.085}{0.15 \times 10^{-3}} = \mathbf{1396 \text{ Wm}^2\text{K}^{-1}}$$

$$\frac{\Delta H_{rxn} R_A^{obs} \rho_{cat} d_p E}{h_p T^2 R} < 0.3$$

$$\frac{\Delta H_{rxn} R_A^{obs} \rho_{cat} d_p E}{T^2 R} = \frac{206.2 \times 3.95 \times 10^{-8} \times 6957 \times 0.15 \times 10^{-3} \times 100}{673^2 \times 8.314}$$

$$= 2.25 \times 10^{-10}$$

$$\frac{\Delta H_{rxn} R_A^{obs} \rho_{cat} d_p E}{h_p T^2 R} = \frac{2.25 \times 10^{-10}}{1396} = 1.6 \times 10^{-13} \ll 0.3$$

So external heat transfer not present

$\lambda_p = 18$ W/m-K for Rh-Ce catalyst

$$\frac{\Delta H_{rxn} R_A^{obs} \rho_{cat} d_p E}{\lambda_p T^2 R} = \frac{2.25 \times 10^{-10}}{18} = 1.25 \times 10^{-11} \ll 3.0$$

So internal heat transfer not present